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TABLE DE MATIÈRES

PREMIÈRE SECTION : **Sciences mathématiques et astronomiques**

PAGES

Sur la géométrie du tétraèdre, par M. V. Thébault 5

Application de la méthode des fonctions majorantes à l'étude de certains systèmes d'équations intégro-différentielles récurrentes, par M. R.H. Germay 13

A propos des fonctions de Bessel à deux variables, par M. P. Humbert. 19

Sur le calcul symbolique à deux variables, par M. N.K. Chakrabarty. 23

DEUXIÈME SECTION : **Sciences physiques et chimiques**

Potential function for the out of the plane vibrations of C_2H_3Br and its seven deuterated substitutes and the effect of anharmonicity on the calculation, by C. Manneback and A. Rahman 28

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Première Section

Sciences Mathématiques et Astronomiques

Sur la géométrie du tétraèdre

PAR

Victor THÉBAULT,
Tennie (France).

A. — Sphères associées a un tétraèdre. — **1.** *Préliminaires.* Après avoir établi quelques propositions générales relatives à un polygone gauche dont n sommets sont cosphériques, nous examinerons ce qu'elles deviennent quand $n = 4$ et en particulier dans le cas où le tétraèdre est orthocentrique.

A chaque sommet A_i, $(i = 1, 2, 3, \ldots, n)$, d'un polygone gauche $(P) \equiv A_1A_2A_3 \ldots A_n$ on fait correspondre le polygone (P_i) déterminé par tous les autres. Soient G le barycentre des sommets A_i de P, G_i celui des sommets de chacun des polygones (P_i). Les points G_i se confondent avec les transformés des points A_i par l'homothétie $\left(G_1 - \frac{1}{n-1}\right)$. (Bellavitis).

Convenons d'appeler $(p) \equiv G_1G_2G_3 \ldots G_n$ polygone *complémentaire* de (P) et désignons par K^2 la somme des carrés des distances des sommets de (P) pris deux à deux de toutes les manières possibles; par K_i^2 la somme analogue des carrés des distances des sommets de (P_i) et par k_i^2 la somme des carrés des $n - 1$ côtés aboutissant au sommet A_i. On obtient

$$K^2 = k_i^2 + K_i^2, \quad \Sigma k_i^2 = 2K^2, \quad \Sigma K_i^2 = (n-2)K^2, \quad \Sigma(k_i^2 + K_i^2) = n.K^2 .$$

D'autre part, d'après une propriété connue,

$$\Sigma \overline{A_iG}^2 = \frac{K^2}{n}, \tag{1}$$

et, d'après le théorème de LEIBNIZ, on a, d'abord,

$$\overline{A_iG}^2 = \frac{1}{n^2}(nk_i^2 - K^2), \tag{2}$$

puis

$$\overline{A_iG_i}^2 = \frac{1}{(n-1)^2}\cdot(nk_i^2 - K^2). \tag{3}$$

En outre, le lieu des points M dont la somme des carrés des distances aux sommets A_i de (P) est égale à la somme K^2 des carrés des distances des sommets pris deux à deux de toutes les manières possibles est une sphère (G, σ_p), de centre G, dont le carré du rayon a pour mesure

$$\sigma_p^2 = \overline{GM}^2 = \frac{1}{n}(K^2 - \Sigma\overline{GA_i}^2) = \frac{n-1}{n^2}\cdot K^2. \tag{4}$$

Les plans perpendiculaires menés du barycentre de $(n-2)$ quelconques des sommets d'un polygone gauche (P) dont les sommets A_i sont sur une sphère (O, R) sur la corde qui passe par les deux sommets restants concourent en un même point Ω *(point de* KANTOR) et les transformés des points de rencontre A_i et A_i' des droites ΩA_i avec la sphère (O, R) par l'homothétie $\left(\Omega, \frac{1}{n-1}\right)$ sont sur une même sphère $\left(o, \frac{R}{n-1}\right)$ transformée de la sphère circonscrite par les homothéties $\left(G, -\frac{1}{n-1}\right)$ et $\left(\Omega, \frac{1}{n-1}\right)$. (Sphère des $3n$ points).

La puissance d'un sommet A_i de (P) par rapport à la sphère des $3n$ points a pour mesure

$$\frac{1}{(n-1)^2}\cdot[(n-1)k_i^2 - K^2]. \tag{5}$$

Enfin, le carré du rayon de la sphère DE LONGCHAMPS [1], de centre Ω, du polygone complémentaire $(\not p)$ de (P) a pour mesure

$$\rho_1^2 = \frac{1}{(n-1)(n-2)^2}\cdot[4(n-1)R^2 - K^2]. \tag{6}$$

---

[1] Pour ce qui est des sphères DE LONGCHAMPS d'un tétraèdre et d'un polygone gauche de n sommets cosphériques que nous avons signalées pour la première fois en 1932 et en 1947, voir *Mathesis*, 1932-223 et *Bull. de la Soc. Royale des Sciences de Liège*, 1947-157.

2. — THÉORÈME. *Les transformées* (a_i, σ_i) *de la sphère* (G, σ_p) *lieu des points dont la somme des carrés de leurs distances aux sommets* G_i *du polygone complémentaire* (p) *d'un polygone gauche* (P) *de n sommets cosphériques est égale à la somme des carrés des distances des sommets de* (p) *pris deux à deux de toutes les manières possibles, par les homothéties* $\left(A_i, \frac{n}{n-2}\right)$, *sont orthogonales à la sphère* DE LONGCHAMPS (Ω, ρ_1) *du polygone* (p).

Car, d'après (4), on a, d'abord,

$$\sigma_p^2 = \sigma_P^2 \cdot \frac{1}{(n-1)^2} = \frac{K^2}{(n-1)\,n^2},$$

puis

$$\sigma_i^2 = \sigma_p^2 \cdot \left(\frac{n}{n-2}\right)^2 = \frac{K^2}{(n-1)\,(n-2)^2}. \tag{7}$$

D'autre part, en observant que

$$a_i\Omega = 2R : (n-2),$$

on obtient l'identité

$$4R^2 = \frac{1}{n-1} \cdot [4\,(n-1)\,R^2 - K^2] + \frac{K^2}{n-1},$$

ce qui achève de démontrer le théorème.

THÉORÈME. — $(n-1)$ *fois la somme des carrés des côtés aboutissant à un même sommet* A_i *d'un polygone gauche* (P), *de n sommets cosphériques diminuées de la somme des carrés des distances des sommets* A_i *pris deux à deux de toutes les manières possibles sont égales à* $(n-1)\,(n-2)^2$ *fois la puissance du sommet considéré par rapport à la sphère* (a_i, σ_i) *correspondante.*

En effet, d'après (6), et, comme en vertu de (2),

$$\overline{A_i a_i}^2 = \overline{A_i G}^2 \cdot \left(\frac{n}{n-2}\right)^2 = \frac{nk_i^2 - K^2}{(n-2)^2},$$

la puissance $\overline{A_i a_i}^2 - \sigma_i^2$ d'un sommet A_i de (P), par rapport à la sphère correspondante (a_i, σ_i), a pour mesure

$$\frac{1}{n-2}\left[\frac{nk_i^2 - K^2}{n-2} - \frac{K^2}{(n-2)\,(n-1)}\right] = \frac{n[(n-1)\,k_i^2 - K]}{(n-1)\,(n-2)^2};$$

d'où la proposition.

COROLLAIRE. — *La sphère de centre* A_i *orthogonale à la sphère* (a_i, σ_i) *coupe aussi orthogonalement la sphère de rayon*

$$\sigma'_i = \frac{R}{n-2}\sqrt{\frac{n}{n-1}} \tag{8}$$

concentrique à la sphère des $3n$ *points du polygone* (P).

Cette propriété résulte des relations (5) et (7).

CAS PARTICULIER. $n = 4$. — *Notations.* Soient un tétraèdre $T \equiv ABCD$ dont les hauteurs sont AA′, BB′, CC′, DD′; (O, R) la sphère circonscrite; G et M le centre de gravité et le point de MONGE; a, a', b, b', c, c' les mesures des arêtes BC, DA, CA, DB, AB, DC dont les milieux sont P, Q, S, U, V, W; R_a, R_b, R_c, R_d les rayons des cercles circonscrits aux faces BCD, CDA, DAB, ABC dont les aires ont pour mesures A, B, C, D.

TÉTRAÈDRE QUELCONQUE T. — Dans cette hypothèse, le lieu des points dont la somme des carrés de leurs distances aux sommets est égale à la somme des carrés des arêtes se confond avec la sphère orthoptique de l'ellipsoïde de STEINER circonscrit à T. Dès lors : *les transformées* (A_1), (B_1), (C_1), (D_1) *de la sphère orthoptique* (G, σ) *de l'ellipsoïde de* STEINER *inscrit au tétraèdre* T *par les homothéties* (A, 2), (B, 2), (C, 2), (D, 2), *sont orthogonales à la sphère de* LONGCHAMPS (M, ρ_1) *du tétraèdre complémentaire t de* T, *de centre* M, *dont le carré du rayon a pour mesure*

$$\rho_1^2 = R^2 - \frac{1}{12}\Sigma(a^2 + a'^2).$$

Car les points A_1, B_1, C_1, D_1 sont symétriques de A, B, C, D par rapport à G et on a, d'abord,

$$A_1M = B_1M = C_1M = D_1M = R\ ,$$

ensuite

$$\overline{A_1M}^2 - \rho_1^2 = R^2 - \rho_1^2 = \frac{1}{12}\Sigma\,(a^2 + a'^2) = \sigma^2.$$

D'autre part, en vertu de (8) : *les sphères* (A), (B), (C), (D) *orthogonales aux sphères* (A_1), (B_1), (C_1), (D_1) *coupent orthogonalement aussi la sphère orthoptique* (O'_{12}) *de la sphère des douze points* (O_{12}) *du tétraèdre* T *et celui-ci est inscrit au tétraèdre déterminé par les plans radicaux de la sphère* (O'_{12}) *associée aux sphères* (A_1), (B_1), (C_1), (D_1).

On obtient aussi, par exemple,

$$D_1A = 2GQ = PQ\,, \tag{9}$$

de sorte que les segments D_1A, D_1B, D_1C sont équipollents aux bimédianes PQ, SU, VW de T et ainsi de suite pour les distances analogues des points A_1, B_1, C_1 aux ternes de sommets correspondants de T. Le tétraèdre $T_1 \equiv A_1B_1C_1D_1$ est inscrit à la sphère (M, R) et ses sommets sont dans les plans médiateurs des hauteurs AA′, BB′, CC′, DD′.

Les puissances des points A, B, C, D par rapport à la sphère (M, R) sont proportionnelles aux quantités

$$(\alpha)=a'^2+b^2+c^2-a^2-b'^2-c'^2,\ (\beta)=a^2+b'^2+c^2-a'^2-b^2-c'^2,$$
$$(\gamma)=a^2+b^2+c'^2-a'^2-b'^2-c^2,\ (\delta)=a'^2+b'^2+c'^2-a^2-b^2-c^2,$$

et le pôle, par rapport à T, du plan radical des sphères (O, R), (M, R) qui se confond avec le plan médiateur du segment OM est sur la courbe d'équation barycentrique

$$\frac{a^2yz}{y+z}+\frac{a'^2xt}{x+t}=\frac{b^2xz}{x+z}+\frac{b'^2yt}{y+t}=\frac{c^2xy}{x+y}+\frac{c'^2zt}{z+t},$$

signalée par M. A. DE MAJO (1) à propos d'une de nos questions et que nous avons étudiée (2). En outre, *la somme des puissances des sommets* A, B, C, D *de* T *pour la sphère* (M, R) *est nulle.*

TÉTRAÈDRE ORTHOCENTRIQUE. — Dans ce cas, d'après (9), on a

$$D_1A = PQ = SU = VW = D_1B = D_1C\,,$$

de sorte que, et par analogie, *les sphères* (A_1), (B_1), (C_1), (D_1) *sont les transformées de la* première *sphère des douze points* (G, σ) *par les homothéties* (A, 2), (B, 2), (C, 2), (D, 2), *et elles se coupent trois par trois aux pieds des hauteurs de* T. Dès lors, en vertu de propriétés connues (3), *les centres* O *et* O_{12} *de la sphère circonscrite et de la* seconde *sphère des douze points de* T *coïncident avec les foyers d'une quadrique de révolution* Σ *inscrite au tétraèdre* T_1; *le centre radical des sphères* (A_1), (B_1), (C_1), (D_1), *est confondu avec l'orthocentre* H *de* T *et la sphère principale relative à l'axe focal de* Σ *est égale à* (O_{12}). D'autre part, les points A_1, B_1, C_1, D_1 coïncident avec les symétriques de A, B, C, D

(1) *Int. des Recherches Mathématiques*, 1947-88.
(2) *The American Mathematical Monthly*, 1950-663.
(3) V. THÉBAULT, *Annales*, 1921-240.

par rapport au centre de gravité G de T, les carrés des rayons des sphères égales (A_1), (B_1), (C_1), (D_1) ont pour mesure

$$R_a^2 + \frac{\overline{AA'}^2}{4} = R_b^2 + \frac{\overline{BB'}^2}{4} = R_c^2 + \frac{\overline{CC'}^2}{4} = R_d^2 + \frac{\overline{DD'}^2}{4},$$

ce qui donne

$$4R_a^2 + \overline{AA'}^2 = 4R_b^2 + \overline{BB'}^2 = 4R_c^2 + \overline{CC'}^2 = 4R_d^2 + \overline{DD'}^2 = 16\sigma^2 = a^2 + a'^2 = b^2 + b'^2 = c^2 + c'^2.$$

Donc, *si deux arêtes opposées d'un tétraèdre* T' *sont égales respectivement à une hauteur et au diamètre du cercle circonscrit à la face correspondante d'un tétraèdre orthocentrique* T, *le tétraèdre* T' *est orthocentrique et ses bimédianes, sa* première *sphère des douze points sont égales à celles de* T.

Autres sphères. Si on désigne par α et α', β et β', γ et γ' les pieds des plus courtes distances des arêtes BC et DA, CA et DB, AB et BC, les droites $\alpha\alpha'$, $\beta\beta'$, $\gamma\gamma'$ passent par H et les sextuples de points (A, B, C, α', β', γ'), (B, C, D', H, β', γ'), (C, A, D', H, γ', α'), (A, B, D', H, α', β') sont situés respectivement sur des sphères (O_d), (O'_d), (O''_d), (O'''_d) centrées sur les normales au plan ABC en les centres des cercles égaux ABC, BCD', CAD', ABD', car, on a, en grandeur et en signe, $DH.DD' = D\alpha'.DA = D\beta'.DB = D\gamma'.DC = 2D\alpha'.DQ = 2D\beta'.DU = 2D\gamma'.DW = \frac{1}{3}[2(a'^2+b'^2+c'^2) - a^2 - b^2 - c^2]$.

Par suite, *la sphère centrée en* D *et orthogonale aux sphères* (O_d), (O'_d), (O''_d), (O'''_d) *rencontre orthogonalement aussi la sphère orthoptique de la* première *sphère des douze points* (G, σ) *du tétraèdre* T.

A chacun des autres sommets A, B, C de T sont associées quatre sphères analogues, ce qui donne seize sphères orthogonales à la sphère orthoptique de la sphère (G, σ), parmi lesquelles quatre ternes de sphères, telles (O'_d), (O''_d), (O'''_d), passent par l'orthocentre H. Les centres des sphères de ces ternes sont dans les plans médiateurs des segments HA', HB', HC', HD'.

Enfin, d'après une propriété connue [1], *le centre radical des sphères* (B, C, D, β, γ, α'), (C, D, A, α, γ, β'), (D, A, B, α, β, γ'), (A, B, C, α', β', γ'), *se confond avec l'orthocentre* H *du tétraèdre* T.

B. — Sur le second point de Lemoine d'un tétraèdre T.

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[1] V. Thébault, *Annales*, 1952-8.

Les *premières* symédianes AL, BL, CL, DL concourent au point L (*second* point de LEMOINE) (1) et percent les faces opposées et la sphère (O, R) circonscrite au tétraèdre T en A_1, B_1, C_1, D_1 et L_a, L_b, L_c, L_d (*associés* de L).

Les coordonnées barycentriques des points L, L_a, L_b, L_c, L_d sont proportionnelles aux quantités

(L)	$ab'c'$,	$bc'a'$,	$ca'b'$,	abc,
(L_a)	$-ab'c'$,	$bc'a'$,	$ca'b'$,	abc,
(L_b)	$ab'c'$,	$-bc'a'$,	$ca'b'$,	abc,
(L_c)	$ab'c'$,	$bc'a'$,	$-ca'b'$,	abc,
(L_d)	$ab'c'$,	$bc'a'$,	$ca'b'$,	$-abc$.

Si l'on pose

$$ab'c' + bc'a' + ca'b' + abc = p_A + p_B + p_C + p_D = S,$$

en appliquant le théorème de STEWART aux distances DD_1, $DA = a'$, DL du sommet D aux points alignés D, L, D_1 dont on connaît le rapport $DL : LD_1$ (1) des distances, puis aux distances AL_d, AL, $AD = a'$ du point A aux points alignés D, L, L_d, on obtient, et par analogie,

$$\overline{DL_d}^2 = \left(\frac{aa' + bb' + cc'}{S - 2p_D}\right).a'b'c', \quad \overline{AL_d}^2 = \left(\frac{-aa' + bb' + cc'}{S - 2p_D}\right).a'bc,$$

$$\overline{BL_d}^2 = \left(\frac{aa' - bb' + cc'}{S - 2p_D}\right).ab'c, \quad \overline{CL_d}^2 = \left(\frac{aa' + bb' - cc'}{S - 2p_D}\right).abc'.$$

De ces formules il résulte la relation

$$(10) \qquad abc.\overline{DL_d}^2 = ab'c'.\overline{AL_d}^2 + bc'a'.\overline{BL_d}^2 + ca'b'.\overline{CL_d}^2,$$

qui constitue une extension du théorème de PTOLÉMÉE au tétraèdre T.

THÉORÈME. — *Les points* L_a, L_b, L_c, L_d *sont les seuls de la sphère circonscrite au tétraèdre* T *à posséder cette propriété.*

En effet, les symédianes AL, BL, CL, DL percent la sphère (O, R) d'équation normale

$$S = \Sigma(a^2BCyz + a'^2DAxt) = 0$$

(1) V. THÉBAULT, *Bull de la Soc. Math. de France*, 1948-100.

en des points de coordonnées normales

$$\frac{x}{-R_a} = \frac{y}{R_b} = \frac{z}{R_c} = \frac{t}{R_d}, \ldots,$$

confondus avec L_a, L_b, L_c, L_d.

Réciproquement, étant donné un point de coordonnées normales (x_1, y_1, z_1, t_1) tel que les points $(-x_1, y_1, r_1, t_1)$, $(x_1, -y_1, z_1, t_1)$, $(x_1, y_1, -z_1, t_1)$, $x_1, y_1, z_1, -t_1)$ sont sur la sphère (O, R), ce point coïncide avec le *second* point de Lemoine L, de T. Car, on a, de proche en proche,

$$O = S(-x_1, y_1, z_1, t_1) = S(x_1, -y_1, z_1, t_1 = \ldots,$$
$$c'^2CDz_1t_1 - c^2ABx_1y_1 = 0, \quad b'^2BDy_1t_1 - b^2CAx_1z_1 = 0,$$
$$a'^2DAx_1t_1 - a^2BCy_1z_1 = 0;$$

d'où

$$C^2b^2c'^2z_1^2 = B^2c^2b'^2y_1^2.$$

Comme x_1, y_1, z_1, t_1 sont de même signe, par hypothèse, il n'y a qu'une solution

$$Cbc'z_1 = Bcb'y_1,$$

soit, et par analogie,

$$z_1bc' \cdot \frac{ca'b'}{R_c} = y_1cb' \frac{bc'a'}{R_b},$$

et

$$\frac{z_1}{R_c} = \frac{y_1}{R_b} = \frac{x_1}{R_a} = \frac{t_1}{R_d}.$$

Si le tétraèdre T est équifacial, la relation (10) se réduit à la suivante,

$$4R^2 = \overline{DL_d}^2 = \overline{AL_d}^2 + \overline{BL_d}^2 + \overline{CL_d}^2.$$

Les associés L_a, L_b, L_c, L_d du *second* point de Lemoine qui coïncide avec le centre de la sphère inscrite, se confondent avec les centres des sphères exinscrites à T et les tétraèdres L_aBCD, L_bCDA, L_cDAB, L_dABC sont trirectangles en L_a, L_b, L_c, L_d.

N. B. — Il y a trois autres points L_1, L_2, L_3 associés au point L, dont nous avons donné les propriétés fondamentales (1).

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(1) *Bull. de la Soc. Math. de France*, loc. cit.

Application de la méthode des fonctions majorantes à l'étude de certains systèmes d'équations intégro-différentielles récurrentes

PAR

R. H. GERMAY

Résumé. — Les résultats démontrés précédemment par la méthode des fonctions majorantes pour les équations intégro-différentielles récurrentes (*) peuvent être complétés en établissant qu'ils se maintiennent pour les *systèmes* de pareilles équations.

§ 1. THÉORÈME. — *Considérons les p suites indéfinies de fonctions de* $p(r+1)+k+1$ *variables complexes*

$$x,\ u_{11},\ \ldots\ u_{p1},\ \ldots\ u_{1,r+1},\ \ldots\ u_{p,r+1},\ w_1,\ \ldots\ w_k$$

savoir

$$(1)\quad F_{j1}\,(x;u_{11},\ldots u_{p1};\ldots u_{1,r+1},\ \ldots u_{p,r+1};\ w_1,\ \ldots w_k),\ F_{j2},\ \ldots F_{j,n},\ldots$$
$$(j=1,\ 2,\ \ldots\ p;\ n=1,\ 2,\ 3,\ \ldots)$$

holomorphes dans les cercles (C), (C_{11}), $\ldots$ (C_{p1}), $\ldots$ $(C_{1,r+1})$, $\ldots$ $(C_{p,r+1})$, (Γ_1), $\ldots$ (Γ_k) *de centres respectifs*

$$x_o, u_{11}^o=y_1^o,\ \ldots u_{p1}^o=y_p^o,\ \ldots u_{1,r+1}^o=y_1^o,\ \ldots u_{p,r+1}^o=y_p^o,\ w_1^o=0,\ \ldots\ w_k^o=0\ ,$$

de rayons respectifs

$$\rho \text{ pour } (C),\ \rho' \text{ pour } (C_{11}),\ \ldots\ (C_{p,r+1}),\ \rho'' \text{ pour } (\Gamma_1)\ \ldots\ (\Gamma_k)$$

et sur les circonférences de ces cercles, c'est-à-dire pour

$$(2)\quad |x-x_o|\leqslant\rho,\ |u_{j1}-u_{j1}^o|\leqslant\rho',\ \ldots\ |u_{j,r+1}-u_{j,r+1}^o|\leqslant\rho',\ |w_i|\leqslant\rho''$$
$$(j=1,\ \ldots\ p,\ l=\ldots k)$$

(*) *Annales de la Société Scientifique de Bruxelles*, t. 66e, série I, pp. 125-130.

Supposons les fonctions F_{jn} *bornées dans leur ensemble dans le champ de variation* (2).

Considérons encore les suites indéfinies de fonctions

$$(3)\quad f_{j,1}^{(l)}(x, s; u_{11}, \ldots u_{p1}; \ldots u_{1,r+1}, \ldots u_{p,r+1}), f_{j,2}^{(l)}, \ldots f_{j,n}^{(l)}, \ldots$$
$$(j = 1, 2, \ldots p; n = 1, 2, \ldots; l = 1, 2, \ldots k)$$

holomorphes dans les cercles

$$(4)\quad |x - x_o| \leqslant \rho\ ,\ |s - x_o| \leqslant \rho\ ,\ |u_{j1} - u_{j1}^o| \leqslant \rho'\ ,\ \ldots\ |u_{j,r+1} - u_{j,r+1}^o| \leqslant \rho'$$
$$(j = 1, 2, \ldots p)$$

et sur leurs circonférences. Supposons-les bornées dans leur ensemble.

Considérons les systèmes d'équations intégro-différentielles récurrentes

$$(5)\quad \frac{dy_{jn}}{dx} = F_{j,n}\left\{\begin{matrix} x;\ y_{1,n}(x), \ldots y_{p,n}(x);\ \ldots y_{1,n+r}(x), \ldots y_{p,n+r}(x) \\ w_{j,n}^{(1)}(x), \ldots\ldots w_{j,n}^{(k)}(x) \end{matrix}\right\}$$
$$(j = 1, \ldots p;\ n = 1, 2, \ldots)$$

où nous avons posé, pour abréger,

$$(6)\quad w_{j,n}^{(l)}(x) = \int_{x_o}^{x} f_{j,n}^{(l)}[x, s; y_{1,n}(s), \ldots y_{p,n}(s); \ldots y_{1,n+r}(s), \ldots y_{p,n+r}(s)]ds$$
$$(l = 1, 2, \ldots k)$$

Pour des valeurs de x *suffisamment voisines de* x_o, *elles définissent un système unique de solutions holomorphes formant* p *suites illimitées*

$$(7)\quad y_{j1} = \varphi_{j1}(x),\ y_{j2} = \varphi_{j,2}(x), \ldots\ y_{jn} = \varphi_{j,n}(x), \ldots\ldots$$
$$(j = 1, \ldots p)$$

et prenant en x_o *les valeurs initiales* y_j^o.

Démonstration

§ 2. — *Construction de développements formels pour les solutions annoncées.* Hormis la complication des calculs, la démonstration est, à des détails près, la même que dans le cas d'équations différentielles récurrentes. Cette remarque nous permettra d'abréger certains raisonnements.

Admettons un instant l'existence et l'holomorphie des solutions annoncées. Pour des valeurs de $|x - x_o|$ suffisamment petites, elles sont développables en séries de Taylor ordonnées suivant les puis-

sances de $(x - x_o)$, savoir

$$(8) \qquad \varphi_{j,n}(x) = c_{j,n}^{(o)} + c_{j,n}^{(1)} \frac{x - x_o}{1!} + \ldots + c_{j,n}^{(q)} \frac{(x - x_o)^q}{q!} + \ldots$$

$$(j = 1, \ldots p), \quad (n = 1, 2, \ldots)$$

Elles donnent lieu aux identités

$$(9) \qquad \varphi_{j,n}(x) = y_j^o + \int_{x_o}^{x} \mathrm{F}_{j,n} \left\{ \begin{matrix} s ; \varphi_{1,n}(s), \ldots \varphi_{p,n+r}(s) ; \\ w_{j,n}^{(1)}(s), \ldots w_{j,n}^{(k)}(s) \end{matrix} \right\} ds$$

moyennant les abréviations

$$(10) \qquad w_{j,n}^{(l)}(s) = \int_{x_o}^{x} f_{j,n}^{(l)} [s, t ; \varphi_{1,n}(t), \ldots \varphi_{p,n+r}(t)] \, dt$$

$$(j = 1, \ldots p ; n = 1, 2, \ldots ; l = 1, 2, \ldots k)$$

Les coefficients $c_{j,n}^{(o)}, \ldots c_{j,n}^{(q)}, \ldots$ ont les valeurs

$$(11) \qquad c_{j,n}^{(o)} = \varphi_{j,n}(x_o) = y_j^o, \ldots c_{j,n}^{(q)} = \left(\frac{d^q \varphi_{j,n}}{dx^q} \right)_{x = x_o}, \ldots$$

Les identités (9) ci-dessus donnent immédiatement

$$(12) \qquad \frac{d\varphi_{j,n}}{dx} = \mathrm{F}_{j,n} [x, \varphi_{1,n}(x), \ldots \varphi_{p,n+r}(x) ; w_{j,n}^{(1)}(x), \ldots w_{j,n}^{(k)}(x)]$$

et par conséquent

$$(13) \qquad \left(\frac{d\varphi_{j,n}}{dx} \right)_{x = x_o} = \mathrm{F}_{j,n} [x_o ; y_1^o, \ldots y_p^o ; \ldots y_1^o, \ldots y_p^o ; 0, \ldots 0]$$

Il vient ensuite

$$(14) \qquad \frac{d^2 \varphi_{j,n}}{dx^2} = \frac{\partial \mathrm{F}_{j,n}}{\partial x} [x, \varphi_{1,n}(x), \ldots w_{j,n}^{(k)}(x)]$$

$$+ \sum_{q=1}^{q=p} \frac{\partial \mathrm{F}_{j,n}}{\partial u_{q1}} \cdot \frac{d\varphi_{q,n}}{dx} + \ldots \sum_{q=1}^{q=p} \frac{\partial \mathrm{F}_{j,n}}{\partial u_{q,r+1}} \cdot \frac{d\varphi_{q,n+r}}{dx} + \sum_{l=1}^{l=k} \frac{\partial \mathrm{F}_{j,n}}{\partial w_l} \cdot \frac{dw_{j,n}^{(l)}}{dx}$$

Par la formule de Leibniz, nous obtenons

$$(15) \qquad \frac{dw_{j,n}^{(l)}}{dx} = \int_{x_o}^{x} \frac{\partial f_{j,n}^{(l)}}{\partial x} [x, s \, \varphi_{1,n}(s), \ldots \varphi_{p,n+r}(s)] \, ds$$

$$+ f_{j,n}^{(l)} [x, x, \varphi_{1,n}(x), \ldots \varphi_{p,n+r}(x)]$$

Il en résulte que

$$(16)\quad \left(\frac{d^2\varphi_{j,n}}{dx^2}\right)_{x=x^o} = \left(\frac{\partial F_{j,n}}{\partial x}\right)_o + \sum_{q=1}^{q=p}\left(\frac{\partial F_{j,n}}{\partial u_{q,1}}\right)_o \cdot (F_{q,n})_o + \dots$$
$$+ \sum_{q=1}^{q=p}\left(\frac{\partial F_{j,n}}{\partial u_{q,r+1}}\right)_o \cdot (F_{q,n+r})_o + \sum_{l=1}^{l=k}\left(\frac{\partial F_{j,n}}{\partial w_l}\right)_o (f_{j,n}^{(l)})_o$$

Les indices o indiquent que les fonctions sont rapportées aux valeurs initiales x_o, y_1^o, ... y_p^o, ... 0, ... 0.

Le calcul des coefficients des développements (8) se poursuit de la même façon. Les formules se compliquent rapidement. Mais l'application répétée du théorème des fonctions composées et celle de la formule de Leibniz n'introduisent que des sommes à coefficients positifs entiers de produits de dérivées des $F_{n,j}$ et des $f_{n,j}^{(l)}$ rapportées aux valeurs initiales x_o, y_1^o, ... y_p^o, ... 0, 0.

Les développements formels (8) peuvent toujours être construits. S'ils convergent, les fonctions qu'ils représentent sont les solutions annoncées des équations données.

§ 3. — *Convergence des développements* (8). Considérons des systèmes d'équations analogues aux systèmes (5)

$$(17)\quad \frac{dY_{j,n}}{dx} = F_{j,n}^*\{x, Y_{1,n}(x), \dots Y_{p,n+r}(x); W_{j,n}^{*(1)}(x), \dots W_{j,n}^{*(k)}(x)\},$$
$$(j = 1, \dots p; n = 1, 2, \dots)$$

où nous avons posé pour abréger

$$(18)\quad W_{j,n}^{*(l)}(x) = \int_{x_o}^{x} f_{j,n}^{*(l)}[x, s; Y_{1,n}(s), \dots Y_{p,n+r}(s)]ds$$
$$(j = 1, \dots p; n = 1, 2, \dots; l = 1, \dots k)$$

Supposons les fonctions holomorphes $F_{j,n}^*$, $f_{j,n}^{*(l)}$ majorantes en x_o, y_1^o, ... y_p^o, ... 0, ... 0 respectivement pour les fonctions $F_{j,n}$ et $f_{j,n}^{(l)}$.

Supposons-les bornées dans leur ensemble. On peut en déduire pour les solutions éventuelles des équations (17) soumises aux conditions initiales indiquées, des développements formels

$$(19)\quad C_{j,n}^{(o)} + C_{j,n}^{(1)}\frac{(x-x_o)}{1!} + \dots + C_{j,n}^{(q)}\cdot\frac{(x-x_o)^q}{q!} + \dots$$
$$(j = 1, \dots p; n = 1, 2, \dots)$$

Ceux-ci sont eux-mêmes majorants pour les développements (8). Leur convergence paraît à première vue aussi difficile à démontrer que celle des séries (8). La difficulté est résolue par un choix convenable des fonctions $F^*_{j,n}$ et $f^{*(l)}_{j,n}$.

D'après nos hypothèses, il existe des nombres positifs fixes M et $\mathfrak{M}$ respectivement supérieurs aux modules des fonctions $F_{j,n}$, $f^{(l)}_{j,n}$ dans les domaines où ces fonctions sont considérées.

Alors, la fonction

$$(20)\qquad \Psi(x, u_{11}, \ldots u_{1r}, \ldots u_{1,r+1}, \ldots u_{p,r+1}, \ldots w_1, \ldots w_k) = \frac{M}{\left(1-\frac{x-x_0}{\rho}\right)\cdot\prod_{j=1}^{j=p}\prod_{l=1}^{l=r+1}\left(1-\frac{u_{j,l}-u^0_{j,l}}{\rho'}\right)\cdot\prod_{t=1}^{t=k}\left(1-\frac{w_t}{\rho''}\right)}$$

est majorante pour toutes les fonctions $F_{j,n}$.

De même, la fonction

$$(21)\qquad \psi(x, s; u_{11}, \ldots u_{p,1}; \ldots u_{1,r+1}, \ldots u_{p,r+1}) = \frac{\mathfrak{M}}{\left(1-\frac{x-x_0}{\rho}\right)\left(1-\frac{s-x_0}{\rho}\right)\cdot\prod_{j=1}^{j=p}\prod_{l=1}^{l=r+1}\left(1-\frac{u_{jl}-u^0_{jl}}{\rho'}\right)}$$

est majorante pour toutes les fonctions $f^{(l)}_{j,n}$. Prenons toutes les fonctions F^*_{jm} égales à Ψ et toutes les fonctions $f^{*(l)}_{jm}$ égales à ψ.

Posons de plus

$$(22)\qquad Y_{j,n}(x) = \eta_{j,n}(x) + y^o_j,\ (j = 1, \ldots p;\ n = 1, 2, \ldots)$$

Toutes les fonctions $\eta_{j,n}(x)$ satisfont à un même système d'équations intégro-différentielles récurrentes; les équations d'un même système sont identiques entre elles; les fonctions η_{jn} se réduisent à zéro pour $x = x_o$; elles sont égales entre elles et leur valeur commune, si elle existe, est la solution $\eta(x)$, nulle en x_o, de l'équation unique

$$(23)\qquad \frac{d\eta}{dx} = \frac{M}{\left(1-\frac{x-x_0}{\rho}\right)\cdot\left(1-\frac{\eta}{\rho'}\right)^{p(r+1)}\cdot w^k}$$

où nous avons posé pour abréger

$$(24)\qquad w = 1 - \frac{1}{\rho''}\int_{x_0}^{x}\frac{\mathfrak{M}ds}{\left(1-\frac{x-x_0}{\rho}\right)\left(1-\frac{s-x_0}{\rho}\right)\left[1-\frac{\eta(s)}{\rho'}\right]^{p(r+1)}}$$

Or, on sait que cette intégrale existe et est holomorphe pour des valeurs de x suffisamment voisines de x_o. Il en résulte que les développements formels (8) convergent effectivement pour de telles valeurs de x et représentent des solutions holomorphes φ_{jn} des équations intégro-différentielles récurrentes (5). Il n'y a pas d'autres solutions jouissant des mêmes propriétés, car les coefficients des séries (8) sont entièrement déterminés par les équations données et par les conditions initiales.

Saive, novembre 1952.

A propos des fonctions de Bessel à deux variables

PAR

M. Pierre HUMBERT

Paul Appell a introduit en 1915 (1) des fonctions nouvelles, qu'il a appelées *fonctions de Bessel à deux variables*, et qui sont définies soit par l'intégrale

$$J_n(x, y) = \frac{1}{\pi}\int_0^{\pi} \cos(nu - x\cos u - y\cos 2u)\, du,$$

soit par la fonction génératrice

$$e^{-\frac{x}{2}\left(u-\frac{1}{u}\right)-\frac{y}{2}\left(u^2-\frac{1}{u^2}\right)} = \sum_{-\infty}^{+\infty} u^n J_n(x, y).$$

Etudiées ensuite par M. Pérés (2), elles ont fait l'objet de travaux très importants de la part de MM. A. Akimov (3) et B. Jekhowsky (4), qui ont pris ces fonctions (étendues à m variables) comme sujets de thèses. Cependant, après ces études exhaustives, ces fonctions sont à peu près tombées dans l'oubli. Il faut avouer que, sauf à quelques problèmes de mécanique céleste, elles ont fort peu d'applications; les formules qui expriment leurs propriétés sont excessivement compliquées; et d'ailleurs ce ne sont pas de véritables fonctions de Bessel, car elles ne se rattachent nullement aux fonctions hypergéométriques. J'ai voulu néanmoins voir si l'application à ces fonctions des règles du calcul symbolique pourrait simplifier leur étude et permettrait d'en obtenir des propriétés nouvelles.

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(1) P. Appell, *C. R. Acad. Sc.*, t. 160, 1915, p. 419.

(2) J. Pérés, *C. R. Acad. Sc.*, t. 161, 1915, p. 168.

(3) A. Akimov, Sur les fonctions de Bessel à plusieurs variables et leurs applications en mécanique (en Russe). Thèse de doctorat, Leningrad, autographiée en 1922, imprimée en 1929.

(4) B. Jekhowsky, Etudes sur les transcendantes Fourier-Bessel à plusieurs variables. Thèse de doctorat, Paris, 1927.

Les fonctions à deux variables s'expriment au moyen des fonctions de Bessel ordinaires par le développement

$$J_n(x, y) = \sum_{K=-\infty}^{+\infty} J_{n-2K}(x)\, J_K(y)$$

Bornons nous à la fonction la plus simple, d'indice zéro : en combinant les termes du développement suivant les valeurs de K, on trouve l'expression (donnée par B. Jekhowsky)

$$J_o(x, y) = J_o(x)\, J_o(y) + 2 \sum_{n=1}^{\infty} J_{4n}(x)\, J_{2n}(y).$$

Introduisons le calcul symbolique, et désignons par p et q les variables symboliques correspondant respectivement à x et y. En utilisant l'image des fonctions de Bessel, on trouve immédiatement

$$J_o(x, y) \supset \frac{pq}{\sqrt{(p^2+1)(q^2+1)}}\left[1 + 2 \sum_{1}^{\infty} \frac{1}{(p+\sqrt{p^2+1})^{4n}\,(q+\sqrt{q^2+1})^{2n}}\right]$$

Pour simplifier l'écriture, posons

$$P = p + \sqrt{p^2+1},\ Q = q + \sqrt{q^2+1},\ r = \sqrt{p^2+1},\ s = \sqrt{q^2+1}.$$

Nous aurons

$$J_o(x, y) \supset \frac{pq}{rs}\left[1 + 2 \sum_{1}^{\infty} \frac{1}{(P^4 Q^2)^n}\right]$$

d'où

$$J_o(x, y) \supset \frac{pq}{rs}\left[1 + 2\left(\frac{1}{1 - \dfrac{1}{P^4 Q^2}} - 1\right)\right]$$

d'où enfin la formule définitive

$$J_o(x, y) \supset \frac{pq}{rs}\,\frac{P^4 Q^2 + 1}{P^4 Q^2 - 1},$$

image qui fait ressortir avec évidence le très grave inconvénient de ces fonctions : leur asymétrie par rapport aux deux variables.

L'application du même procédé nous conduira assez facilement aux images suivantes, que nous écrivons avec les mêmes notations :

$$J_1(x, y) \supset \frac{pq}{rs}\,\frac{P\,(P^2Q^2 - P^2Q - Q - 1)}{P^4Q^2 - 1},$$

$$J_2(x, y) \supset \frac{pq}{rs}\,\frac{P^2\,(P^2Q - PQ + Q^2 + P)}{P^4Q^2 - 1}.$$

On pourrait trouver ainsi l'image de la fonction générale : mais la complication de ces premières images ne permet guère d'espérer que le calcul symbolique puisse apporter une grande aide dans l'étude de ces fonctions.

Dans un cas particulier, cependant, on peut obtenir une formule qui paraît nouvelle. Revenant à la fonction d'ordre zéro, remplaçons x par $2\sqrt{t}$ et y par t. On aura, d'après le développement signalé plus haut,

$$J_o(2\sqrt{t}, t) = J_o(2\sqrt{t})\, J_o(t) + 2 \sum_1^\infty J_{4n}(2\sqrt{t})\, J_{2n}(t).$$

Or l'image du second membre est assez simple. On sait en effet que [1]

$$J_m(t)\, J_{2m}(2\sqrt{t}) \supset \frac{p}{\sqrt{p^2+1}}\, e^{-\frac{p}{p^2+1}}\, J_m\left(\frac{1}{p^2+1}\right)$$

On aura donc

$$J_o(2\sqrt{t}, t) \supset \frac{p}{\sqrt{p^2+1}}\, e^{-\frac{p}{p^2+1}} \left[J_o\left(\frac{1}{p^2+1}\right) + 2 \sum_1^\infty J_{2n}\left(\frac{1}{p^2+1}\right)\right]$$

Mais il est bien connu que le crochet ci-dessus est égal à l'unité : On a donc l'image relativement simple :

$$J_o(2\sqrt{t}, t) \supset \frac{p}{\sqrt{p^2+1}}\, e^{-\frac{p}{p^2+1}}.$$

Cherchons à transformer cette image par le théorème du produit. Partons de

$$e^{-\frac{1}{p}} - 1 \subset J_o(2\sqrt{t}) - 1$$

d'où, par dérivation,

$$p e^{-\frac{1}{p}} - p \subset -\frac{J_1(2\sqrt{t})}{\sqrt{t}}$$

Appliquons à cette correspondance la transformation (*loc. cit.*, p. 17)

$$\frac{p}{p^2+1}\, \varphi\left(\frac{p^2+1}{p}\right) \subset \int_o^t J_o\left[2\sqrt{x\,(t-x)}\right] f(x)\, dx.$$

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[1] McLachlan, Humbert et Poli, Supplément au formulaire pour le calcul symbolique (*Fasc.* CXIII *du Mémorial*), p. 42.

il vient

$$e^{-\frac{p}{p^2+1}} - 1 \subset -\int_0^t J_0\left[2\sqrt{x\,(t-x)}\right] J_1\left(2\sqrt{x}\right) \frac{dx}{\sqrt{x}}. \qquad (A)$$

Soit à présent

$$\frac{p}{\sqrt{p^2+1}} \subset J_0(t)$$

d'où

$$\frac{p^2}{\sqrt{p^2+1}} - p \subset -J_1(t) \qquad (B)$$

et appliquons le théorème du produit à (A) et (B) :

$$\frac{1}{p}\cdot\left(\frac{p^2}{\sqrt{p^2+1}} - p\right)\left(e^{-\frac{p}{p^2+1}} - 1\right) \subset \int_0^t d\lambda\, J_1(t-\lambda) \int_0^\lambda J_0\left[2\sqrt{x(\lambda-x)}\right] J_1\left(2\sqrt{x}\right) \frac{dx}{\sqrt{x}}$$

Or le premier membre est égal à

$$\frac{p}{\sqrt{p^2+1}}\, e^{-\frac{p}{p^2+1}} - \frac{p}{\sqrt{p^2+1}} - \left(e^{-\frac{p}{p^2+1}} - 1\right),$$

et son original est

$$J_0\left(2\sqrt{t}, t\right) - J_0(t) + \int_0^t J_0\left[2\sqrt{x\,(t-x)}\right] J_1\left(2\sqrt{x}\right) \frac{dx}{\sqrt{x}}.$$

d'où, en rapprochant les deux dernières formules, et en posant dans l'intégrale simple $x = t\cos^2\theta$, dans l'intégrale double $x = \lambda\cos^2 u$ et $\lambda = t\cos^2 v$, on trouve le résultat que nous avions en vue :

$$J_0\left(2\sqrt{t}, t\right) = J_0(t) - 2\sqrt{t}\int_0^{\frac{\pi}{2}} J_0(t\sin 2\theta)\, J_1\left(2\sqrt{t}\cos\theta\right)\sin\theta\, d\theta$$

$$- 4t\sqrt{t}\int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} J_0(t\sin 2u\cos^2 v)\, J_1(t\sin^2 v)\, J_1\left(2\sqrt{t}\cos u\cos v\right)\cos^2 v\sin v\sin u\, du$$

Cette formule est fort compliquée : mais avec les fonctions de Bessel à deux variables, il ne faut jamais s'attendre à des résultats simples.

Sur le calcul symbolique à deux variables

PAR

N. K. CHAKRABARTY
(présenté par M. Pierre Humbert)

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1. — Soient, avec les notations habituelles,

$$\varphi\ (p,\ q) \subset\subset f(x,\ y)$$

l'image et l'original dans le calcul symbolique à deux variables, de sorte que l'on a

$$\varphi\ (p, q) = pq \int_0^\infty \int_0^\infty e^{-px-qy} f\ (x, y)\ dx\ dy$$

Pour justifier, dans la suite, les changements dans l'ordre d'intégration, nous utiliserons une extension d'un théorème de La Vallée Poussin (1), sous la forme suivante : si l'on a

$$\begin{aligned} h\ (u, v, x, y) &= h_1\ (u, v, x, y)\ \psi_1\ (x, y) \\ &= h_2\ (u, v, x, y)\ \psi_2\ (u, v), \end{aligned}$$

et si l'on a les conditions suivantes :

1° $h_1\ (u, v, x, y)$ est borné pour $x \geqslant 0,\ y \geqslant 0,\ 0 \leqslant u \leqslant b_1,\ 0 \leqslant u \leqslant b_2$

2° $h_2\ (u, v, x, y)$ est borné pour $u \geqslant 0,\ v \geqslant 0,\ 0 \leqslant x \leqslant a_1,\ 0 \leqslant y \leqslant a_2,$

3° $\int_0^\infty \int_0^\infty \psi_1\ (x, y)\ dx\ dy$ et 4° $\int_0^\infty \int_0^\infty \psi_2\ (u, v)\ du\ dv$

sont convergents, alors on pourra écrire

$$\int_0^\infty \int_0^\infty du\ dv \int_0^\infty \int_0^\infty h(u,v,x,y)\ dx\ dy = \int_0^\infty \int_0^\infty dx\ dy \int_0^\infty \int_0^\infty h(u,v,x,y)\ du\ dv$$

2. — *Théorème* I. — On a

$$f(x^2, y^2) \supset\supset \frac{pq}{\pi} \int_0^\infty \int_0^\infty e^{-\frac{p^2 s^2}{4} - \frac{q^2 t^2}{4}} \varphi\left(\frac{1}{s^2}, \frac{1}{t^2}\right) ds\, dt$$

(sous réserve de la convergence de l'intégrale).

On a en effet $\varphi(p, q) \subset\subset f(x, y)$

d'où

$$st\, \varphi\left(\frac{1}{s}, \frac{1}{t}\right) = \int_0^\infty \int_0^\infty e^{-\frac{x}{s} - \frac{y}{t}} f(x, y)\, dx\, dy$$

Multipliant les deux membres par $\dfrac{e^{-as-bt}}{st\sqrt{st}}$, avec $a>0$, $b>0$, puis intégrant par rapport à s et t, puis changeant l'ordre des intégrations, on obtient

$$\int_0^\infty \int_0^\infty e^{-as-bt} \varphi\left(\frac{1}{s}, \frac{1}{t}\right) \frac{ds\, dt}{\sqrt{st}}$$

$$= \int_0^\infty \int_0^\infty f(x, y)\, dx\, dy \left[\int_0^\infty \frac{e^{-as-\frac{x}{s}}}{s\sqrt{s}} ds \int_0^\infty \frac{e^{-bt-\frac{y}{t}}}{t\sqrt{t}} dt\right]$$

Or

$$\int_0^\infty \frac{e^{-as-\frac{x}{s}}}{s\sqrt{s}} ds = \sqrt{\frac{\pi}{x}}\, e^{-2\sqrt{ax}}$$

donc, après réduction,

$$\int_0^\infty \int_0^\infty e^{-\frac{p^2 s^2}{4} - \frac{q^2 t^2}{4}} \varphi\left(\frac{1}{s^2}, \frac{1}{t^2}\right) ds\, dt$$

$$= \pi \int_0^\infty \int_0^\infty e^{-px-qy} f(x^2, y^2)\, dx\, dy$$

d'où le théorème proposé.

On notera que la démonstration est licite si $f(x, y)$ est de l'ordre de x^{μ_1} pour x petit, et de y^{μ_2} pour y petit, μ_1 et μ_2 étant positifs, et si a, b, x, y, sont positifs.

Comme applications, sans en indiquer la démonstration, nous remarquerons simplement que l'on peut en tirer les images suivantes :

$$x^{2\lambda} y^{2\mu}\, {}_r F_{s+2}(\alpha_1, \ldots, \alpha_r; \beta_1, \ldots, \beta_s, \lambda+1, \mu+1; x^2 y^2)$$

$$\supset\supset \frac{\Gamma(2\lambda+1)\, \Gamma(2\mu+1)}{p^{2\lambda} q^{2\mu}}\, {}_{r+2}F_s\left(\alpha_1, \ldots, \alpha_r, \lambda+\frac{1}{2}, \mu+\frac{1}{2}; \beta_1, \ldots, \beta_s; \frac{16}{p^2 q^2}\right)$$

Introduisant les fonctions de Bessel, on aura

$$\frac{\sqrt{\pi}}{2^{\nu}\Gamma\left(\nu+\frac{1}{2}\right)}\,y^{\nu}\,I_{\nu}(\sqrt{2xy})\,J_{\nu}(\sqrt{2xy}) \supset\supset \frac{p^{\nu+1}\,q}{(1+p^2q^2)^{\nu+\frac{1}{2}}},$$

avec $R(\nu) > -\frac{1}{2}$.

Introduisant ensuite la « Bessel Product Function » de Costello, (2) définie par

$$X_n^b(x) = ber_n^2(x) + bei_n^2(x),$$

on aura

$$\frac{X_n^b(2\sqrt{ixy})}{y} \supset\supset (-1)^{\frac{n}{2}}\frac{q}{n.2^n}(\sqrt{p^2q^2+4}-pq)^n,$$

Enfin, introduisant la fonction de Bessel d'ordre trois (3), on aura

$$J_{o,o}(3\sqrt[3]{x^2y^2}) \supset\supset \frac{pq}{4\sqrt{\pi}}\,e^{\frac{p^2q^2}{32}}\,K_o\left(\frac{p^2q^2}{32}\right).$$

3. — *Théorème* II. Si $\varphi(u, v) \subset\subset h(x, y)$ et $g(x) \supset \psi(u)$,

alors

$$\int_o^{\infty}\frac{\varphi(u,v)\;g(u)}{uv}\,du = \int_o^{\infty}\int_o^{\infty}\frac{h(x,y)\;\psi(x)}{x}\,e^{-vy}\,dx\,dy.$$

Les conditions exigées seront : $h(x, y)$ de l'ordre de x^{μ_1} pour x petit, et y^{μ_2} pour y petit, μ_1 et μ_2 positifs, et de l'ordre de $e^{-x\lambda_1}$ pour x grand, et $e^{-y\lambda_2}$ pour y grand, λ_1 et λ_2 positifs; et de même pour $g(x)$ quand x est petit ou grand.

La démonstration du théorème est aisée.

On pourra en tirer les valeurs de diverses intégrales doubles : contentons nous de citer

$$\int_o^{\infty}\int_o^{\infty} e^{-vy}\,I_o(\sqrt{2xy})\,J_o(\sqrt{2xy})\,\frac{dx\,dy}{\sqrt{1+x^2}} = \frac{1}{v}\,I_o\left(\frac{1}{2v}\right)K_o\left(\frac{1}{2v}\right).$$

4. — L'application du « théorème du produit », c'est-à-dire de la formule (4)

$$\frac{1}{pq}\varphi_1(p, q)\,\varphi_2(p, q) \subset\subset \int_0^x\int_0^y f_1(x-\lambda, y-\rho)\, f_2(y, \rho)\, d\lambda\, d\rho$$

$$= \int_0^x\int_0^y f_1(\lambda, \rho)\, f_2(x-\lambda, y-\rho)\, d\lambda\, d\rho$$

où $f_1(x, y) \supset\supset \varphi_1(p, q)$ et $f_2(x, y) \supset\supset \varphi_2(p, q)$, nous permet de trouver diverses images. Soient les fonctions *ster* et *stei* [5], définies par

$$ster\,(x) + i\,stei\,(y) = H_o\,(xi^{\frac{3}{2}})$$

où H_o est la fonction de Struve d'ordre zéro.

On a

$$H_o\,(2\sqrt{xy}) \supset\supset \frac{\sqrt{pq}}{1+pq}$$

d'où

$$ster\,(2\sqrt{xy}) \supset\supset \frac{1}{\sqrt{2}}\,\frac{\sqrt{pq}\,(1+pq)}{1+p^2q^2}$$

$$stei\,(2\sqrt{xy}) \supset\supset \frac{1}{\sqrt{2}}\,\frac{\sqrt{pq}\,(1-pq)}{1+p^2q^2}$$

donc

$$ster\,(2\sqrt{xy}) + stei\,(2\sqrt{xy}) \supset\supset \sqrt{2}\,\frac{\sqrt{pq}}{1+p^2q^2}$$

$$ster\,(2\sqrt{xy}) - stei\,(2\sqrt{xy}) \supset\supset \sqrt{2}\,\frac{pq\sqrt{pq}}{1+p^2q^2}$$

Mais on a

$$ber\,(2\sqrt{xy}) \supset\supset \frac{p^2q^2}{1+p^2q^2}$$

$$bei\,(2\sqrt{xy}) \supset\supset \frac{pq}{1+p^2q^2}$$

D'où, par application du théorème de produit,

$$\int_0^x\int_0^y ber\,(2\sqrt{xy})\,dx\,dy \supset\supset \frac{1}{pq}\cdot\frac{p^2q^2}{1+p^2q^2} \subset\subset bei\,(2\sqrt{xy})$$

$$\int_0^x \int_0^y [ster\,(2\sqrt{xy}) - stei\,(2\sqrt{xy})]\,dx\,dy \supset\supset \sqrt{2}\,\frac{1}{pq}\cdot\frac{pq\sqrt{pq}}{1+p^2q^2}$$

$$\subset\subset ster\,(2\sqrt{xy}) + stei\,(2\sqrt{xy})$$

Et, comme

$$\frac{\sqrt{pq}}{1+p^2q^2} = \frac{1}{pq}\cdot\frac{1}{\sqrt{pq}}\frac{p^2q^2}{1+p^2q^2},$$

on aura

$$\int_0^x \int_0^y (x-\lambda)^{\frac{1}{2}}(y-\rho)^{\frac{1}{2}}\,ber\,(2\sqrt{\lambda\rho})\,d\lambda\,d\rho$$

$$= \frac{\pi}{4\sqrt{2}}[ster\,(2\sqrt{xy}) + stei\,(2\sqrt{xy})]$$

Plusieurs intégrales ou images analogues pourront être obtenues de la même façon.

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Deuxième Section

Sciences Physiques et Chimiques

Potential function for the out of the plane vibrations of C_2H_3Br and its seven deuterated substitutes and the effect of anharmonicity on the calculation

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PART I. — SYNOPSIS

The dimensions of the molecule C_2H_3Br are taken to be C — H distances = 1.07 Å. CCH angles = 120°, C — C distance 1.34 Å with C — Br distance = 1.891 Å and C — Br angle = 121°42′, so as to give the observed accurate moments of inertia; still remaining within the limits of the electron diffraction data, the last three can be allowed small variations so that the moments of inertia can be reproduced showing the uncertainty inherent in this way of fixing the dimensions.

A study of the isotopic ratios of the 8 molecules in the isotopic set leads to a satisfactory attribution of frequencies where this is doubtful; it also gives an idea of the effect of anharmonicity in the observed frequencies.

The theory of the out of the plane vibrations with infinitesimal amplitude leads to the identities recently published by Decius and

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Wilson ([2]); from these identities the values of the three diagonal coefficients and the squares of the three non-diagonal coefficients are obtainable unambiguously provided the data available has already been corrected for anharmonicity. The sign of the non-diagonal coefficients can then be fixed by using one of the several equations which involve odd powers of these constants.

By considering that the observed frequencies, in this problem, will all be stepped up by varying degrees throughout the isotopic set when the anharmonicity has been corrected for, it is shown for example that the values of the diagonal constants obtained by using directly the observed data will be less than their true value.

The excellent nature of the experimental data available on the infra-red absorption in the vapour state for the whole isotopic set is exhibited by the fact that the above mentioned identities are well satisfied by this data. We also get some idea of the differential anharmonicity in going from one molecule of the set to another.

Starting off with such high quality data, the calculation shows that the numerical values of the coefficients are not obtained with the same degree of certainty, this being specially true of the non-diagonal constants one of which is given with an uncertainty of nearly 25 % (when the most pessimistic view is taken of the distribution of the minute uncertainties in the initial data).

An important result of the calculation is that with the data provided the signs of the non-diagonal constants cannot be fixed in a straightforward and certain manner. The only way to make the assignment is found to be the ' empirical ' way of seeing which combination gives the best possible set of calculated frequencies. The numerical values of these coefficients being considerable there is no ambiguity in this way of fixing the signs because a wrong selection obviously leads to a calculated set of frequencies very widely different from the observed set.

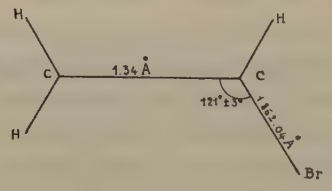
1. — Introduction

The gauche (i. e. out of the plane) vibrations of mono-bromo-ethylene (or vinyl bromide) and the 7 isotopic molecules obtained by the substitution of deuterium have already been the object of study by Van Hamme in an unpublished thesis ([1]). The experimental data available at that time (1944) was, as compared to the present position extremely incomplete and as the detailed calculation of

Van Hamme showed it was not possible to calculate the potential function on the basis of the data then available. The theoretical part of his work contains certain relations between the potential constants and the frequencies of the 8 molecules in the isotopic set; these relations, now called the sum rules, were reported recently in a systematic and general form, by other workers in the field. The present paper is thus the first detailed application of the newly published rules of Decius and Wilson ([2]), ([2a]), and shows clearly the extent to which they are useful in the calculation of the potential function.

2. — Dimensions of the molecule C_2H_3Br

In the tables compiled by Allen and Sutton ([3]) giving molecular structures analysed by electron diffraction, we find the following data :



The electron diffraction experiments are able to give us information only regarding the heavy nuclei. Thus even the C — C distance had to be assumed to have the value 1.34 Å. In the following calculations the positions of the H were fixed according to the following scheme

(1) all C — H distances = 1.07 Å

(2) all $\widehat{CCH}$ angles = 120°

(3) the C — C distance = 1.34 Å

We shall denote the C — Br distance by R, the $\widehat{CCBr}$ angle by θ and the C — C distance by L.

Accurate analysis of the pure rotation spectrum of the molecule in the microwave region has enabled Cornwell ([4]) to give the following values for the principal moments of inertia :

$C_2H_3Br^{79}$ has $I_B = 121.43$, $I_C = 130.83$ and $I_A = I_C - I_B$

$C_2H_3Br^{81}$ has $I_B = 122.14$, $I_C = 131.55$ and $I_A = I_C - I_B$

Obviously the major contribution to the moments of inertia arises from the heavy ' skeleton ' of the molecule consisting of the two carbons and Br. With L_1 assumed to be 1.34 Å, θ and R can be used as parameters whose values can be chosen so as to give the experimental I_A, I_B and I_C for C_2H_3Br. This is a straightforward though long computation; with $\theta = 121°42'$ and $R = 1.891$ Å (the masses being $m_H = 1.008132$, $m_D = 2.014726$, $m_C = 12.00388$ and $m_{Br} = 79.916$, as throughout this paper), we get $I_B = 121.7985$ and $I_C = 131.2048$ while the experimental values averaged with Br^{79} and Br^{81} are $I_B = 121.785$ and $I_C = 131.19$

L_1, the distance C — C, obviously plays considerable role in determining the moments of inertia of the molecule. Assuming any other value for L_1 requires a readjustment of θ and R to give the observed moments of inertia. As a trial, C — C was increased by 1 % being taken to be 1.353; then to give the required I_B and I_C we must have $R = 1.879$ Å and $\theta = 122°6'$, the rest being, as before, C — H distances 1.07 Å and $\widehat{CCH}$ angles 120°. The two sets

$$C—C = 1.34 \text{ Å}, \widehat{CCBr} = 121°42', \quad C — Br = 1.891 \text{ Å}$$

and

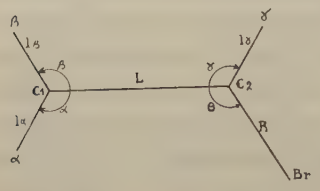
$$C—C = 1.353 \text{ Å}, \widehat{CCBr} = 122°6', \quad C — Br = 1.879 \text{ Å}$$

are equally good from the point of view of the experimental errors in the electron diffraction data; both lie within the experimental error given *.

It may be mentioned that the « isotopic ratio », to use an accepted terminology, of the molecules C_2H_3Br and C_2D_3Br, also does not give us any indication as to which of the two sets of dimensions given above is preferable. In this paper we have adopted the first set given above.

(*) CHARETTE and DE HEMPTINNE [5] have used the values $\theta = 121°$ and R = 1.86 Å, the most probable experimental values of Allen and Sutton; thus their values of the moments of inertia of C_2H_3Br do not coincide with the highly accurate values of Cornwell. In this paper we have tried to reproduce Cornwell's moments of inertia while remaining within the experimental uncertainties of the electron diffraction data.

3. — Nomenclature of the molecules in the isotopic series

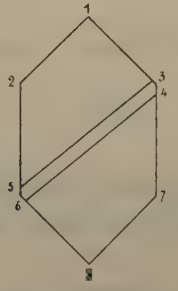


$l_\alpha = l_\beta = l_\gamma = 1.07$ Å $= l$ (say)
$\alpha = \beta = \gamma = 120°$
L $= 1.34$ Å, R $= 1.891$ Å
$\theta = 121°42'$

1.	H_α,	H_β,	H_γ	5.	H_α,	D_β,	D_γ
2.	H_α,	H_β,	D_γ	6.	D_α,	H_β,	D_γ
3.	H_α,	D_β,	H_γ	7.	D_α,	D_β,	H_γ
4.	D_α,	H_β,	H_γ	8.	D_α,	D_β,	D_γ

Molecules 3 and 4 differ in an exchange of H and D between positions α and β and are chemically inseparable. The same is true for 5 and 6.

Rayleigh's rule regarding the shift of all frequencies to lower values when the mass at one spot of the vibrating system is increased makes us focus attention on a series formed out of the above eight so that in going from one to the other in the series we have just one H replaced by a D. The following diagram shows all possible series of the kind.



There are thus six possible ladders by which one can descend from the lightest to the heaviest molecule. Rayleigh's rule must be satisfied for each one of these ladders.

4. — Experimental results in infra-red absorption and attribution of frequencies

The complete spectrum of the whole isotopic set has now been published by Charette and de Hemptinne [5]; the unpublished results were very kindly furnished to us. The data is homogeneous in so far as it has been obtained throughout by the infra-red absorption in the vapour state. The identification of the gauche frequencies depends on the fact that a movement out of the plane induces an

electric moment perpendicular to the plane (which is the direction of maximum moment of inertia) giving rise to typical C-bands in the spectrum. Out of the 24 frequencies only one is missing but this has been taken from the Raman spectrum. This is not completely satisfactory, the Raman spectrum having been obtained in the liquid state, but considering that this is just one in a set of 24, we cannot regard it as a serious defect. The following are the observed frequencies in cm^{-1}. The experimental accuracy is ± 1 cm^{-1}.

1.	583	902	942	5. 6.	476	690.5	855.5
2.	551	802	906		531.5	719	872
3. 4.	484.5	793	918(R)	7.	465	724	871
	541	811	940	8.	462	691	731.5

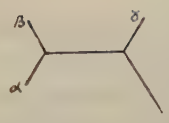
The assignment of the frequencies in the mixed data of 3,4 and 5,6 is partly accomplished by making use of Rayleigh's rule for frequency shift. Applying this to the step $3 \to 5$ and $4 \to 6$ we see that 484.5 and 476 go together i. e. if 484.5 belongs to 3 then 476 must belong to 5.

We immediately see that the data is certainly defective in one spot. In passing from (5,6) to 8 the frequency 690.5 increases to 691 which is contrary to Rayleigh's rule. But the two are equal to each other within the experimental error and hence we can overlook this defect.

The complete assignment can however be accomplished either by means of the ratio of the product of the three frequencies which is independent of the force system of the molecule or by means of the sum-rules which shall be elaborated elsewhere in this paper. The final attribution is given in table I together with λ_i the *squares* of frequencies reduced with the factor $(1303.06\ldots)^2 = 1697965$ (*). The table also gives the sum of squares, the sum of products of squares taken in pairs and the products of squares, all reduced with the above factor. These are denoted respectively by S, P and Δ.

(*) When frequency ν is given in cm^{-1}, the force constant f in 10^5 dynes per cm and the mass m in terms of 1 /16 of the mass of O^{16} as unit i.e. 1.65972×10^{-24} *gm* we get $\frac{\nu^2}{(1303.06)^2} = \frac{f}{m}$. In other words 1303.06 cm^{-1} is the frequency of oscillation of an oscillator of mass 1.65972×10^{-24} *gm* under a force whose constant of proportionality is 10^5 dynes per cm. The physical constants used are those proposed by Dumond and Cohen (6).

TABLE I



	λ_1	λ_2	λ_3	S	P	Δ
1. H_α, H_β, H_γ	583	902	942	1.20193	0.45094	0.050126
	0.20017	0.47916	0.52260			
2. H_α, H_β, D_γ	551	802	906	1.04103	0.33729	0.032743
	0.17880	0.37881	0.48342			
3. H_α, D_β, H_γ	484.5	811	940	1.04600	0.32707	0.027867_5
	0.13825	0.38736	0.52039			
4. D_α, H_β, H_γ	541	793	918 (Raman)	1.03874	0.33304	0.031665
	0.17237	0.37035	0.49602			
5. H_α, D_β, D_γ	476	719	872	0.88572	0.23673	0.018193_5
	0.13344	0.30446	0.44782			
6. D_α, H_β, D_γ	531.5	690.5	855.5	0.87820_5	0.23946	0.020137
	0.16637	0.28080	0.43103			
7. D_α, D_β, H_γ	465	724	871	0.88285	0.23414	0.017564
	0.12734	0.30871	0.44679			
8. D_α, D_β, D_γ	462	691	731.5	0.72205	0.16358	0.11140
	0.12570_5	0.28121	0.31514			

4*a*. — The isotopic ratios and the Teller-Redlich rule

The rule for the isotopic ratios is useful as a means to throw light on the assumed dimensions of the molecule and on the attribution of frequencies to different molecules of the set where such attribution is doubtful. Further, this rule also gives an indication of the amount of anharmonicity in the observed frequencies. The gist of the rule is that $(\Delta_i/\Delta_j)^{1/2}$, which can be obtained from the observed frequencies of molecules i and j of the set and also from the assumed dimensions, should be such that when j is heavier compared with i, the theoretical value of the ratio should be greater than that obtained experimentally.

For relevant references we shall mention here Herzberg's « Polyatomic Molecules », where is also given the necessary formula which here becomes

$$\left(\frac{\Delta_i}{\Delta_j}\right)^{1/2}_{\text{theoretical}} = \left[\frac{(m_\alpha m_\beta m_\gamma)_j}{(m_\alpha m_\beta m_\gamma)_i} \times \frac{(M)_i}{(M)_j} \times \frac{(I_A \times I_B)_i}{(I_A \times I_B)_j}\right]^{1/2}$$

where M denotes the total mass of the molecule.

Table II gives the principal moments of inertia of the 8 molecules; these are necessary for an evaluation of $(\Delta_i/\Delta_j)^{1/2}$ from the above formula. A and B are the principal axes in the molecular plane while C is the perpendicular axis. The unit of length is the Angstrom and that of mass is 1.65972×10^{-24} gm.

TABLE II

Mol	$I_A + I_B = I_C$	$I_A \times I_B$	Mol	$I_A + I_B = I_C$	$I_A \times I_B$
1	131.2048	1145.671	5	146.0082	1594.532
2	135.6984	1472.267	6	141.6695	1773.966
3	141.6191	1244.421	7	147.4815	1534.275
4	137.1972	1417.129	8	151.8720	1916.721

Calling « adjacent » those molecules in which just one nucleus differs in mass (m_H or m_D), the possible pairs of adjacent molecules are (1, 2), (1, 3), (1, 4), (2, 5), (2, 6), (3, 5), (3, 7), (4, 6), (4, 7), (5, 8), (6, 8), (7, 8). These can be obtained directly by a glance at the figure given in section 3. The following isotopic ratios are obtained for these pairs of adjacent molecules :

TABLE III

(i, j)	$\left(\frac{\Delta i}{\Delta j}\right)^{1/2}_{exp}$	$\left(\frac{\Delta i}{\Delta j}\right)^{1/2}_{theo}$	δ the diff in %
(1,2)	1.237	1.241	0.3
(1,3)	1.341	1.348	0.5
(1,4)	1.258	1.265	0.6
(2,5)	1.342	1.352	0.7
(2,6)	1.276	1.282	0.5
(3,5)	1.238	1.245	0.6
(3,7)	1.260	1.269	0.7
(4,6)	1.254	1.258	0.3
(4,7)	1.343	1.353	0.7
(5,8)	1.278	1.284	0.5
(6,8)	1.344	1.354	0.7
(7,8)	1.256	1.259	0.2

Before we discuss certain regularities in the twelve ratios given in table III, let us first see the behaviour of the 7 isotopic ratios $(\Delta_1/\Delta_j)^{1/2}$, $j = 2, 3, \ldots, 8$. These are

TABLE IV

j	exp	theo	δ in %	
2	1.237	1.241	0.3	with 2 of m_H and 1 of m_D
3	1.341	1.348	0.5	
4	1.258	1.265	0.6	
5	1.660	1.678	1.1	with 1 of m_H and 2 of m_D
6	1.578	1.591	0.9	
7	1.689	1.711	1.3	
8	2.121	2.154	1.5	with 3 of m_D

The systematic behaviour of δ in table III where it remains in the neighbourhood of 0.5 % throughout is certainly satisfactory since each pair differs in the change of an m_H to an m_D at just one place. Also as is expected, table IV shows the pronounced effect of anharmonicity as the ' distance ' of the molecule increases from molecule 1, the lightest. The δ for 2, 3, 4 is in the neighbourhood of 0.5 %, of 5, 6, 7 about 1 % and for 8 it is 1.5 %. This is obviously due to the persistence of δ in the neighbourhood of 0.5 % in table III.

We conclude that the dimensions assumed are not too far off the mark and that the attribution of frequencies is also correct.

4*b*. — The data on overtones

The usefulness of this data in evaluating the anharmonic correction depends upon our ability to form accurately the differences such as e. g. (the observed first overtone frequency) — 2 (the observed fundamental frequency). A consideration of the frequencies supplied, which have an accuracy of $\pm$ 1 cm^{-1}, shows that the available data on overtones cannot be so useful. Hence for the purposes of the present paper we regard as given,the observed fundamental frequencies without possibility of being corrected for anharmonicity with the help of available data on overtones which is not reproduced here.

5. — The theory of vibrations with infinitesimal amplitude

If we denote by **Q** a set of internal coordinates for the vibrating system and by **q** a set of external coordinates then **Q** and **q** will be

related by the equation $\mathbf{Q} = \rho\mathbf{q}$ whene ρ is a rectangular matrix with more columns than rows.

Let the potential energy V, of vibration about the position of stable equilibrium be given by $2V = \mathbf{Q}'\mathbf{F}\mathbf{Q}$ where $\mathbf{F}$ is a symmetric matrix and let the kinetic energy T in terms of $\mathbf{q}$ be $2T = \dot{\mathbf{q}}'\mathbf{M}\dot{\mathbf{q}}$ where $\mathbf{M}$ is also symmetric. A primed vector, or matrix being written for its transpose.

Then it is easily shown that the *squares* of frequencies of normal vibrations, say λ_1, λ_2, λ_3 are given by the determinantal equation $[\mathbf{GF} - \lambda\mathbf{I}] = 0$ where $\mathbf{G} = (\rho\mathbf{M}^{-1}\rho')$ and $\mathbf{I}$ is the identity matrix. $\mathbf{G}$ above is the usual ' G-matrix ' of Wilson.

For the problem under consideration we regard the plane of the molecule at rest as the *xy* plane and the six displacements out of this plane as the components of $\mathbf{q}$. They are z_α, z_β, z_γ, z_{C_1}, z_{C_2}, z_{Br} in that order. The kinetic energy is given by $2T = \Sigma m_i \dot{z}_i^2$.

For $\mathbf{Q}$ we choose the displacements of α, β and γ out of the plane formed by the instantaneous positions of C_1, C_2 and Br (throughout we shall refer to this as the « skeleton plane ») viz. Q_α, Q_β, Q_γ, and write the potential energy V in terms of a symmetric matrix as follows

$$2V = (Q_\alpha Q_\beta Q_\gamma) \begin{pmatrix} f_{11} & f_{12} & f_{13} \\ f_{12} & f_{22} & f_{23} \\ f_{13} & f_{23} & f_{33} \end{pmatrix} \begin{pmatrix} Q_\alpha \\ Q_\beta \\ Q_\gamma \end{pmatrix}$$

The matrix ρ specifying the relation between $\mathbf{Q}$ and $\mathbf{q}$ is

$$\rho \equiv \begin{pmatrix} 1 & 0 & 0 & (-1+p-s)/2 & (-1+p+s)/2 & -p \\ 0 & 1 & 0 & (-1-p+r)/2 & (-1-p-r)/2 & p \\ 0 & 0 & 1 & (-1-p+s)/2 & (-1-p-s)/2 & p \end{pmatrix}$$

$$p = (l/R)\ (\sin 120^\circ/\sin\theta),\ s + r = 2p\{1 - 2(R/L)\cos\theta\}$$

$$s - r = 2\{1 - 2(l/L)\cos 120^\circ\}.$$

While $\mathbf{M}^{-1}$ is simply a diagonal matrix with $1/m_i$ occurring along the diagonal.

For brevity let us partition ρ into two parts $\rho \equiv (\rho_1 \mid \rho_2)$, ρ_1 being the first three columns of ρ and hence just the identity. Similarly $\mathbf{M}^{-1}$ can be partitioned into four parts as

$$\mathbf{M}^{-1} \equiv \left(\begin{array}{c|c} \mu_1 & \mathbf{O} \\ \hline \mathbf{O} & \mu_2 \end{array}\right) \text{ where}$$

$$\mu_1 \equiv \begin{pmatrix} 1/m_\alpha & 0 & 0 \\ 0 & 1/m_\beta & 0 \\ 0 & 0 & 1/m_\gamma \end{pmatrix} \text{ and } \mu_2 \equiv \begin{pmatrix} 1/m_{C_1} & 0 & 0 \\ 0 & 1/m_{C_2} & 0 \\ 0 & 0 & 1/m_{Br} \end{pmatrix}$$

The matrix $\mathbf{G} = \rho \mathbf{M}^{-1} \rho'$ is thus simply $\mu_1 + \rho_2 \mu_2 \rho_2'$. The masses m_α, m_β, m_γ occur only along the diagonal of $\mathbf{G}$. We write $\mathbf{G}$ as

$$\begin{pmatrix} g_{11} + (1/m_\alpha) & g_{12} & g_{13} \\ g_{12} & g_{22} + (1/m_\beta) & g_{23} \\ g_{13} & g_{23} & g_{33} + (1/m_\gamma) \end{pmatrix}$$

The secular equation thus becomes

$$\begin{vmatrix} (f_{11}/m_\alpha) + h_{11} - \lambda & (f_{12}/m_\alpha) + h_{12} & (f_{13}/m_\alpha) + h_{13} \\ (f_{12}/m_\beta) + h_{21} & (f_{22}/m_\beta) + h_{22} - \lambda & (f_{23}/m_\beta) + h_{23} \\ (f_{13}/m_\gamma) + h_{31} & (f_{23}/m_\gamma) + h_{32} & (f_{33}/m_\gamma) + h_{33} - \lambda \end{vmatrix} = 0$$

which can be expanded into $\Delta - P\lambda + S\lambda^2 - \lambda^3 = 0$, with roots λ_1, λ_2, λ_3, so that

$$S = \lambda_1 + \lambda_2 + \lambda_3, \quad P = \lambda_2 \lambda_3 + \lambda_3 \lambda_1 + \lambda_1 \lambda_2, \quad \Delta = \lambda_1 \lambda_2 \lambda_3$$

Our aim is to calculate the f_{ij}, all other quantities being available from experimental data. The solution is immediate and simple due to the peculiar form of the secular determinant. This determinant when expanded gives the following S, P and Δ.

$$S = f_{11}/m_\alpha + f_{22}/m_\beta + f_{33}/m_\gamma + h_{11} + h_{22} + h_{33} \tag{1}$$

$$P = f_{22}f_{33}/m_\beta m_\gamma + f_{22}h_{33}/m_\beta + f_{33}h_{22}/m_\gamma + h_{22}h_{33} - f_{23}^2/m_\beta m_\gamma - f_{23}h_{32}/m_\beta - f_{23}h_{23}/m_\gamma - h_{23}h_{32}$$

$$+ \ldots\ldots \quad + \ldots\ldots \tag{2}$$

$$\Delta = |\mathbf{G}|\,|\mathbf{F}| \tag{3}$$

Denoting by S_j, P_j, Δ_j the quantities referring to the $j'th$ molecule of the isotopic set, we get the following identities (4), (5) and (6) from (1), (2) and (3) respectively.

$$\left.\begin{aligned} S_1 - S_4 = S_2 - S_6 = S_3 - S_7 = S_5 - S_8 = (1/m_H - 1/m_D) f_{11} \\ S_1 - S_3 = S_2 - S_5 = S_4 - S_7 = S_6 - S_8 = (1/m_H - 1/m_D) f_{22} \\ S_1 - S_2 = S_3 - S_5 = S_4 - S_6 = S_7 - S_8 = (1/m_H - 1/m_D) f_{33} \end{aligned}\right\} \tag{4}$$

$$\left.\begin{aligned} P_1 - P_3 - P_4 + P_7 = P_2 - P_5 - P_6 + P_8 = (1/m_H - 1/m_D)^2 (f_{11}f_{22} - f_{12}^2) \\ P_1 - P_4 - P_2 + P_6 = P_3 - P_7 - P_5 + P_8 = (1/m_H - 1/m_D)^2 (f_{33}f_{11} - f_{13}^2) \\ P_1 - P_2 - P_3 + P_5 = P_4 - P_6 - P_7 + P_8 = (1/m_H - 1/m_D)^2 (f_{22}f_{33} - f_{23}^2) \end{aligned}\right\} \quad (5)$$

$$\Delta_1/|G_1| = \Delta_2/|G_2| = \ldots\ldots = \Delta_8/|G_8| = |F| \quad (6)$$

The identities (4) and (5) are special cases of the rules of Decius and Wilson ([2]) and (6) is simply an equivalent formulation of the well known rule of Teller and Redlich for isotopic ratios. Hence a knowledge of the λ_i for all the 8 molecules gives the whole of **F** without difficulty. The sign of f_{ij}, $i \neq j$, which remains undetermined in using (4) and (5) only, is fixed by the equations (1), (2) or (3).

This completes the determination of **F**. A re-evaluation of λ_i through the **F** so found and the appropriate **G**, by solving $|\mathbf{GF} - \lambda\mathbf{I}| = 0$ should give the λ_i through which **F** was evaluated, and hence the frequencies $(\lambda_i)^{1/2}$.

6. — The effect of imperfections in data and of anharmonicity

Needless to say that for the actual experimentally given values of λ_i, i. e. of S_j, P_j and Δ_j, none of the above identities will be perfectly satisfied.

As regards the effect of experimental errors we can say that in view of the large number of observations supplied, the overall effect of the experimental inaccuracies will be very much smoothed out; also since the data supplied is intrinsically of relatively high precision we can expect that whatever defects there do exist are not of great importance.

The effect of anharmonicity on the other hand is of quite a different character. It is not a random effect but a systematic one. As is well known, the heavier the component nuclei of a molecule relatively less will be the effect of anharmonicity on the frequencies of normal vibrations. Nevertheless, qualitatively the anharmonicity plays the same role in varying the normal frequencies of vibration throughout the eight molecules of the set. As is generally true for all non-degenerate vibrations the zero-order frequencies (i. e. harmonic frequencies) are higher than the actually observed frequencies of vibration, thus the observed frequencies when corrected for anharmonicity will all be stepped up, this increase being relatively more marked the lighter the molecule.

It is then immediately seen that the f_{ii} calculated from observed frequencies by using the identities (4) in article 5 will be systematically *less* than the true values. On the other hand the same cannot be said of difference $(f_{ii}\, f_{jj} - f_{ij}^2)$ since the identities out of which they are obtained involve four quantities of which the most and the least affected by anharmonicity are positive and those affected by an amount in between are negative.

As will be shown in this paper the knowledge of the observed frequencies uncorrected for anharmonicity places a definite limit on the amount of information obtainable from the identities (4) *and* (5) *even though at first sight they seem to give a ready and an immediate tool for a complete evaluation of the f_{ii} and the f_{ij}; this important result being specially significant in the determination of the latter.*

7. — Application of sum and product rules to the observed data

We shall write $(1/m_{\text{H}} - 1/m_{\text{D}}) = k = 0.4955882$. Then from table I

$$\left.\begin{aligned} S_1 - S_4 &= 0.16319 \\ S_2 - S_6 &= 0.16282 \\ S_3 - S_7 &= 0.16315 \\ S_5 - S_8 &= 0.16367 \end{aligned}\right\}$$ All the four quantities should have been equal, each being equal to kf_{11}.

We notice that the identities are very nearly satisfied. The average is 0.16321 and the maximum dispersion is only about ± 0.0004 or about $\pm 1/4$ % of the average.

At this point our difficulties start appearing. First let us consider the effect of allowing an error of $\pm$ 1 cm^{-1} in the observed frequencies. This is on the average about $\pm$ 0.3 % in the *squares* of the frequencies leading to a dispersion of about $\pm$ 0.003 in the values of S_1, S_2, S_3 and S_4 and of about $\pm$ 0.002 in those of S_5, S_6, S_7 and S_8. This gives for the differences $S_i - S_j$ a dispersion at the worst of about $\pm$ 0.005. Thus apart from anharmonicity, only from uncertainty in the experimental data we can expect a dispersion of $\pm$ 0.005 in the values of $S_i - S_j$ given above i. e. the satisfaction of the required identities can be affected to the extent of $\pm$ 3 % due to an error of $\pm$ 1 cm^{-1} (i. e. $\sim$ 0.15 %) in the observed frequencies. (Obviously one has $0.15 \times 2 \times 10 = 3$, the factor 2 for the squaring and 10 for the taking of the difference). But as stated above the dispersion

in the identities is only $\pm$ 1/4 % which is about 1 order of magnitude smaller than the expected $\pm$ 3 %. This is a clear proof that

(i) as far as the satisfaction of the above identities is concerned, the experimental data can be regarded as dispersionless, and

(ii) what dispersion there does exist in the identities is not valuable as a guide to any other source of dispersion (e. g. anharmonicity) since it is impossible to eliminate that part of it which arises out of the possible defects in the experimental data.

As regards the effect of anharmonicity it is now obvious that within the uncertainty allowed by experiment we have throughout the S values of the isotopic set the same differential anharmonicity. In other words from the behaviour of the dispersion in the identities given above, we cannot hope to get any information on anharmonicity.

This argument perhaps enables us to say that the experimental errors are small enough so that the last figure in each experimental datum is correct, i. e. the error is not of $\pm$ 1 cm^{-1} but only of $\pm$ 0.5 cm^{-1} and also that on the whole it is fairly random.

With the above remarks applying to the case of kf_{22} and kf_{33} given below, we proceed with the calculations. We have

$S_1 - S_3 = 0.15593$
$S_2 - S_5 = 0.15531$
$S_4 - S_7 = 0.15587$
$S_6 - S_8 = 0.15616$

Each should be equal to kf_{22}. The average is 0.15582. The maximum dispersion is about $\pm$ 1/3 %.

$S_1 - S_2 = 0.16090$
$S_3 - S_5 = 0.16028$
$S_4 - S_6 = 0.16053$
$S_7 - S_8 = 0.16080$

Each should be equal to kf_{33} The average is 0.16063. The maximum dispersion is about $\pm$ 1/4 %.

This gives us :

$f_{11} = 0.3293$
$f_{22} = 0.3144$
$f_{33} = 0.3241$

$\pm$ 0.0008

We repeat the remark already made that the effect of anharmonicity on these values is *definitely* to make them smaller than what they actually are. The amount by which this is happening can perhaps be qualitatively stated as equal to the differential anharmonic effect on the S of adjacent molecules of the set. Moreover we cannot afford to forget completely the effect of the experimental inaccuracies even though at this stage it is really very insignificant. As will be

seen, at a later stage of the calculation the experimental inaccuracies are very far from being altogether ignorable.

In the calculation of the f_{ij}, or more precisely at this stage of the f_{ij}^2 we encounter greater difficulties. We have from table I

$$\left.\begin{aligned} P_1 - P_3 - P_4 + P_7 &= 0.02497 \\ P_2 - P_5 - P_6 + P_8 &= 0.02468 \end{aligned}\right\} \quad \text{Each being } k^2 (f_{11}f_{22} - f_{12}^2)$$

$$\left.\begin{aligned} P_1 - P_4 - P_2 + P_6 &= 0.02007 \\ P_3 - P_7 - P_5 + P_8 &= 0.01978 \end{aligned}\right\} \quad \text{Each being } k^2 (f_{33}f_{11} - f_{13}^2)$$

$$\left.\begin{aligned} P_1 - P_2 - P_3 + P_5 &= 0.02331 \\ P_4 - P_6 - P_7 + P_8 &= 0.02302 \end{aligned}\right\} \quad \text{Each being } k^2 (f_{22}f_{33} - f_{23}^2)$$

The dispersion from the average in each case is about $\pm 3/4$ %; here again it is taking place at least one order of magnitude within the latitude allowed by experimental error. The same remarks as we have made above again hold good; we cannot hope to get information regarding anharmonicity from the above figures. In fact one should take a still more pessimistic view because each of the quantities above is a small difference of large quantities and inspite of that is no guide towards the effect of anharmonicity that one might have expected to see through its behaviour.

Now let us calculate f_{ij}^2 because we already know f_{ii}. We have

$$\begin{aligned} k^2 (f_{22}f_{33} - f_{23}^2) &= (0.02316 \pm 0.00015) \\ \text{or } k^2 f_{23}^2 &= -0.02316 \pm 0.00015 + (k f_{22})(k f_{33}) \\ &= -0.02316 \pm 0.00015 + 0.02503 \pm 0.00014 \\ &= 0.00187 \pm 0.00029 \end{aligned}$$

Even though matters will slightly improve in taking the square root, we can see how very much the f_{23} so calculated will be affected by an almost negligible dispersion in the data of frequencies supplied; the above figures show that such a tiny initial dispersion can lead to a value of f_{23} differing by as much as ± 8 %. Even though the quantities on the right hand side are apparently so trustworthy, their near equality places the value of their difference in comparatively much greater doubt. But at least one point appears to be justifiably made, it being that the actual f_{23}^2 (i. e. $|f_{23}|$) must be greater than the value here obtained; this is so because, as we have already mentioned, the nature of the identities (5) through which $k^2(f_{ii}f_{ij} - f_{ij}^2)$ are obtained will be most probably unaffected by anharmonicity while those through which kf_{ii} are obtained are

definitely affected in a particular way. Hence we may expect that of the two numbers 0.02503 and 0.02316 used above to find f_{23}^2, the former will be increased when corrected for anharmonicity while the latter (at least relatively speaking) will remain unaffected, thus increasing the value of their difference, i. e. of f_{23}^2.

Consider now f_{13}^2 and f_{12}^2. We have

$$k^2 (f_{33} f_{11} - f_{13}^2) = 0.01997 \pm 0.00015$$
$$\text{or } k^2 f_{13}^2 = -0.01997 \pm 0.00015 + 0.02622 \pm 0.00014$$
$$= 0.00625 \pm 0.00029$$

i. e. $|f_{13}|$ is determined with an uncertainty of about 3 %.

$$k^2 (f_{11} f_{22} - f_{12}^2) = 0.02483 \pm 0.00015$$
$$\text{or } k^2 f_{12}^2 = -0.02483 \pm 0.00015 + 0.02543 \pm 0.00014$$
$$= 0.00060 \pm 0.00029$$

An almost negligible dispersion in the data can thus affect the calculated $|f_{12}|$ to the surprising amount of ± 25 %. Thus the uncertainty is most marked for f_{12}, least for f_{13}. *We can say that the effect of using the observed frequencies without being corrected for anharmonicity is to give the values of f_{ii} and of $|f_{ij}|$ systematically less than their actual value. We can also say that this reduction will be, in terms of percentage, only a unit or two in the f_{ii} but much more marked in the f_{ij}.*

The values of the f_{ij} are from the above figures, the following

$$f_{23} = \pm (0.087 \pm 0.007)$$
$$f_{31} = \pm (0.160 \pm 0.005)$$
$$f_{12} = \pm (0.050 \pm 0.012).$$

Thus the uncertainty in the calculated values of the f_{ij} does *not* arise because of their magnitude which as seen above is not negligible compared to the f_{ii}.

8. — Attribution of signs to the f_{ij}; building of the G matrix

As explained in section 5, the signs of f_{ij} $i \neq j$, which remain undetermined by the solution obtained from identities (4) and (5), can be fixed by using either of equations (1), (2) or (3).

But as in section 7, the use of observed frequencies uncorrected for anharmonicity again produces difficulties. This is really very surprising because as already mentioned the absolute values of the

f_{ij} are far from being negligible. A difficulty in the fixation of sign when the quantity is numerically small is not unexpected but in the present case it is really surprising.

This article has two widely different headings. We have put the two together because we start making actual use of the **G** matrices for the molecules only at this stage. Up to now the peculiar nature of the secular determinant enabled us to eliminate the elements of **G** involving the dimensions of the molecule from equations (1) and (2) to determine f_{ii} and f_{ij}^2. But now we need the **G** matrix. According to the notation of section 5 the various quantities g_{ij} are as follows :

$$g_{11} = 0.4458430,\ g_{12} = g_{21} = 0.07322307,\ g_{13} = g_{31} = -0.4105174$$
$$g_{22} = 0.1132543,\ g_{23} = g_{32} = 0.05806419$$
$$g_{33} = 0.5418047$$
$$\text{and } 1/m_{\text{H}} = 0.9919336 \text{ and } 1/m_{\text{D}} = 0.4963454,$$

so that **G** for any molecule of the set is obtained by using $1/m_{\text{H}}$ or $1/m_{\text{D}}$ in the appropriate place along the diagonal together with g_{ii} as has been shown in section 5.

The **G** matrices of molecules 1 and 8 are as follows

$$\begin{pmatrix} 1.437777 & 0.07322307 & -0.4105174 \\ 0.07322307 & 1.105188 & 0.05806419, \\ -0.4105174 & 0.05806419 & 1.533738 \end{pmatrix}$$

$$\begin{pmatrix} 0.9421884 & 0.07322307 & -0.4105174 \\ 0.07322307 & 0.6095997 & 0.05806419 \\ -0.4105174 & 0.05806419 & 1.038150 \end{pmatrix}$$

Those for the other molecules are simply different combinations of the rows and columns of the above two.

We have mentioned in section 5 that Teller and Redlich rule is alternatively expressible in terms of the ratios $|\mathbf{G}_i|/|\mathbf{G}_j|$. As expected $|\mathbf{G}_1|/|\mathbf{G}_8|$ from above is $(2.2343)/(0.48130) = 4.642$ while in the form expressed by Teller and Redlich it is $(2.154)^2 = 4.640$.

Now to return to the problem of fixing the signs of the f_{ij}. First let us consider equation (1) of section 5, for the molecules 1 and 8.

$$S_1 = 1.43778\, f_{11} + 1.10519\, f_{22} + 1.53374\, f_{33} + \\ + (0.14645\, f_{12} + 0.11613\, f_{23} - 0.82103\, f_{31})$$
$$S_8 = 0.94219\, f_{11} + 0.60960\, f_{22} + 1.03815\, f_{33} + \\ + (0.14645\, f_{12} + 0.11613\, f_{23} - 0.82103\, f_{31})$$

Using the values of f_{ii} and the observed S_1, S_8 we get

$$0.14645 f_{12} + 0.11613 f_{23} - 0.82103 f_{31} = 1.2019 \pm 0.003 - 1.3180 \pm 0.003$$
$$= -0.1161 \pm 0.006$$
$$0.14645 f_{12} + 0.11613 f_{23} - 0.82103 f_{31} = 0.7221 \pm 0.002 - 0.8384 \pm 0.002$$
$$= -0.1163 \pm 0.004$$

The agreement on the right hand side is nothing new. It is implicit in the fact that the sum rules are well obeyed throughout the set. Let us take

$$0.14645 f_{12} + 0.11613 f_{23} - 0.82103 f_{31} = -0.1162 \pm 0.005$$

It is immediately obvious that f_{31} must be positive. Putting $f_{31} = +0.160 \pm 0.005$, we get

$$0.14645 f_{12} + 0.11613 f_{23} = -0.1162 \pm 0.005 + 0.1314 \pm 0.004$$
$$= +0.0152 \pm 0.009$$

Naturally we do not hope that the values of f_{12} and f_{23} already found will satisfy this equation; in fact the very presence of an uncertainty in the values of f_{12} and f_{23} we have, together with that on the right hand side of the above equation makes such a hope an absurdity. But what we do hope to get out of the above equation is some guidance as to the selection of the signs of f_{12} and f_{23} which are yet to be determined. We write the above equation as

$$0.15 f_{12} + 0.12 f_{23} = \left\{ \begin{array}{c} +0.024 \\ +0.006 \end{array} \right\}$$

the right hand showing the latitude allowed due to dispersion. Allowing for the uncertainty in the values of f_{12} and f_{23} we find that the left hand side

(i) when $f_{12}>0$, $f_{23}>0$, will be between 0.0153 and 0.0203
(ii) when $f_{12}<0$, $f_{23}>0$, will be between 0.0003 and 0.0056
(iii) when $f_{12}>0$, $f_{23}<0$, will be between — 0.0056 and — 0.0003
(iv) when $f_{12}<0$, $f_{23}<0$, will be between — 0.0203 and — 0.0153

The evidence is not conclusive; still it seems to indicate that the order in which the four cases have been listed is the order in which they may be prefered for the purpose of satisfying the equation as best as possible.

Thus, as stated already at the beginning of this article, we come to the surprising conclusion that fairly accurate experimental data

when uncorrected for anharmonicity prevents us from fixing in a decisive way the signs of all the f_{ij} even though the numerical values of these may be far from being negligible.

The use of equation (3) of section (5) is also possible for fixing the signs of the f_{ij}. In view of the numerical verification that follows in section 9 a separate treatment of equation (3) seems unprofitable. To be exhaustive however let us see the actual figures. This equation is

$$\Delta = |\mathbf{G}|\,|\mathbf{F}|$$

Now $|\mathbf{G}_1| = 2.2343$ and $|\mathbf{G}_8| = 0.48130$ and the observed $\Delta_1 = 0.05013 \pm 0.0004$ and $\Delta_8 = 0.01114 \pm 0.0001$ allowing for an error of $\pm$ 1 cm^{-1} in the observed data.

$$\therefore |\mathbf{F}| \text{ (from 1)} = 0.02243 \pm 0.0002$$
$$|\mathbf{F}| \text{ (from 8)} = 0.02314 \pm 0.0002$$

The discrepancy is nothing but the anharmonicity and has already been discussed in section 4*a*. It is interesting to see that an extreme application of experimental uncertainty in bringing the values nearer will still leave a discrepancy due to anharmonicity; in case of random experimental errors however such an extreme point of view is really not admissible. Now

$$|\mathbf{F}| = (f_{11}f_{22}f_{33}) - (f_{11}f_{23}^2 + f_{22}f_{31}^2 + f_{33}f_{12}^2) + 2f_{23}f_{31}f_{12}$$

and we have

$$\left.\begin{matrix} f_{11} = 0.3293 \\ f_{22} = 0.3144 \\ f_{33} = 0.3241 \end{matrix}\right\} \pm 0.0008, \qquad \left.\begin{matrix} f_{23}^2 = 0.0076 \pm 0.0013 \\ f_{31}^2 = 0.0256 \pm 0.0016 \\ f_{12}^2 = 0.0025 \pm 0.0012 \end{matrix}\right\} f_{31} = +0.160 \pm 0.005$$

This gives $f_{11}f_{22}f_{33} = 0.03354 \pm 0.00025$ and $(f_{11}f_{23}^2 + f_{22}f_{31}^2 + f_{33}f_{12}^2) = 0.01136 \pm 0.0013$.

$$\therefore |\mathbf{F}| = f_{12}f_{23}(0.320 \pm 0.010) + (0.03354 \pm 0.00025) - (0.01136 \pm 0.0013)$$
$$= f_{12}f_{23}(0.320 \pm 0.010) + (0.02218 \pm 0.0015)$$

$\therefore$ From molecule 1, $f_{12}f_{23}(0.320 \pm 0.010) = 0.00025 \pm 0.0017$
and From molecule 8, $f_{12}f_{23}(0.320 \pm 0.010) = 0.00097 \pm 0.0017$

Obviously the right hand side means nothing i. e. the sign of the product $f_{12} \times f_{23}$ cannot be decided on the basis of equation (3) of section 5.

These circumstances compel us to fall back on a procedure which,

though not entirely satisfactory, at least does enable us to state clearly what the signs should be. The test of the accuracy of a potential function is, finally, always that when the secular determinant is set up with this potential and the appropriate geometry its solution should give us the observed frequencies with a tolerable degree of dispersion allowing for the experimental errors as well as for the uncorrected anharmonicity. This statement being accepted, if in the potential function we choose wrongly the sign of a coefficient whose absolute value is not negligible then the calculated frequencies will be far beyond the allowed degree of dispersion. We use this method to decide whether we must have

$$\left.\begin{matrix} f_{12} = +0.050 \\ f_{23} = +0.087 \end{matrix}\right\} \quad \text{or} \quad \left.\begin{matrix} -0.050 \\ +0.087 \end{matrix}\right\} \quad \text{or} \quad \left.\begin{matrix} +0.050 \\ -0.087 \end{matrix}\right\} \quad \text{or} \quad \left.\begin{matrix} -0.050 \\ -0.087 \end{matrix}\right\}$$

9. — Assignment of signs to f_{12} and f_{23} by actual calculation of frequencies

Using the **G** matrix given already for molecules 1 and 8, and the **F** formulated above we get the results given in table V.

We need not consider the case when both f_{12} and f_{23} are taken negative for it will obviously give a solution with a large negative error. There now remains no doubt regarding the assignment of signs to these two coefficients. We must take $f_{12} = +(0.050 \pm 0.012)$ and $f_{23} = -(0.087 \pm 0.007)$ and certainly $f_{31} = +(0.160 \pm 0.005)$ of which there never was any doubt.

It must be mentioned however that table V on the basis of which the decision has been made ignores the fact that these coefficients have been obtained with a certain degree of uncertainty (this being as high as $\pm$ 25 % in the case of $[f_{12}]$. But it is to be expected that when we take account of this dispersion there will not result any change in the decision already made. The following leaves no doubt on this matter. Since in the above table taking $f_{12} = -0.050$, $f_{23} = +0.087$ gives a set of frequencies which, taken together, are too low we can make full use of the allowed dispersion by taking $f_{12} = -0.038$ and $f_{23} = +0.094$ to get all possible help to improve the calculated frequencies.

On calculation this gives :

for molecule 1, $\lambda^3 - 1.192\,\lambda^2 + 0.4359\,\lambda - 0.04689 = 0$

TABLE V

Expansion of the secular determinant and its roots together with observed values of squares of frequencies.

$\begin{pmatrix} 0.3293 & +0.050 & +0.160 \\ +0.050 & 0.3144 & -0.087 \\ +0.160 & -0.087 & 0.3241 \end{pmatrix}$	$\begin{pmatrix} 0.3293 & -0.050 & +0.160 \\ -0.050 & 0.3144 & +0.087 \\ +0.160 & +0.087 & 0.3241 \end{pmatrix}$	$\begin{pmatrix} 0.3293 & +0.050 & +0.160 \\ +0.050 & 0.3144 & +0.087 \\ +0.160 & +0.087 & 0.3142 \end{pmatrix}$	F
$\lambda^3 - 1.1839\,\lambda^2 + 0.43469\,\lambda - 0.046524 = 0$	$\lambda^3 - 1.1894\,\lambda^2 + 0.43486\,\lambda - 0.04650 = 0$	$\lambda^3 - 1.2042\,\lambda^2 + 0.44807\,\lambda - 0.052720 = 0$	Mol 1
λ_1 λ_2 λ_3	λ_1 λ_2 λ_3	λ_1 λ_2 λ_3	
0.1880 0.4755 0.5204	0.1895 0.4324 0.5675	0.2623 0.3267 0.6150	calc.
0.2002 0.4792 0.5226	0.2002 0.4792 0.5226	0.2002 0.4792 0.5226	exper.
— 6 % — 1.0 % — 0.5 %	— 5 % — 10 % + 9 %	+ 30 % — 30 % + 18 %	
$\lambda^3 - 0.70423\,\lambda^2 + 0.15455\,\lambda - 0.010022 = 0$	$\lambda^3 - 0.70980\,\lambda^2 + 0.15492\,\lambda - 0.010016 = 0$	$\lambda^3 - 0.72448\,\lambda^2 + 0.16312\,\lambda - 0.011357 = 0$	Mol 8
λ_1 λ_2 λ_3	λ_1 λ_2 λ_3	λ_1 λ_2 λ_3	
0.1163 0.2782 0.3097	0.1172 0.2480 0.3446	0.1388 0.2301 0.3556	calc.
0.1257 0.2812 0.3151	0.1257 0.2812 0.3151	0.1257 0.2812 0.3151	exper.
— 7,5 % — 1.0 % — 1.6 %	— 7 % — 13 % + 9 %	+ 10 % — 18 % + 13 %	

with roots and errors 0.193 (— 3.5 %), 0.420 (— 12.5 %), 0.579 (+11 %)
for molecule 8, $\lambda^3 - 0.7124\ \lambda^2 + 0.1557\ \lambda - 0.01010 = 0$
with roots and errors 0.118 (—6 %), 0.245 (—13 %), 0.349 (+11 %)
which shows that allowance for the uncertainty in the numerical values of f_{12} and f_{23} does not change the qualitative nature of the result. It is needless to verify this for any other way of allowing the dispersion.

The above calculations show conclusively that the signs of f_{ij}, $i \neq j$ should be as in the following :

$$\begin{pmatrix} 0.3293 & +0.050 & +0.160 \\ +0.050 & +0.3144 & -0.087 \\ +0.160 & -0.087 & 0.3241 \end{pmatrix}$$

of course the numerical value of each of the six being subject to certain uncertainties already mentioned. At the moment we are concerned over their signs not their numerical values.

The above manner of fixing the signs is certainly not the most satisfactory but in view of the discussion given in section 8, seems to be the only appropriate one. In section 15 of this paper, we shall see how the attribution of signs to the $f_{ij}\ i \neq j$ will affect the coefficients in the potential function when the latter is written in terms of the motion of certain structural units of which the molecule is composed.

One instructive remark can be made at this stage; the initial data has a certain dispersion which leads to much larger dispersion in the f_{ii} and f_{ij}. Naturally the frequencies recalculated on the basis of such a potential will give values which have a certain uncertainty of their own. An example of this occurs above. While

$$\begin{pmatrix} 0.3293 & -0.050 & +0.160 \\ -0.050 & 0.3144 & +0.087 \\ +0.160 & +0.087 & +0.3241 \end{pmatrix}$$ gives 0.190, 0.432, 0.568 for 1 and 0.117, 0.248, 0.345 for 8

$$\begin{pmatrix} 0.3293 & -0.038 & +0.160 \\ -0.038 & 0.3144 & +0.094 \\ +0.160 & +0.094 & 0.3241 \end{pmatrix}$$ gives 0.193, 0.420, 0.579 for 1 and 0.118, 0.245, 0.349 for 8

a change of about 0.5 to 1.0 % in the frequencies (the above are squares). The initial data has an average accuracy of 1 in 750 or perhaps slightly better which shows that *when the cycle of computation (involving several small differences in large quantities) is rounded the uncertainty in the calculated set of frequencies, in terms of percentage,*

is in this case about one order of magnitude worse than the dispersion of the initial data. This aspect of the problem will be dealt with more satisfactorily in section 10.*a.* of this paper. Let us remark however that there is nothing new in the conclusion emphasised above; it is a well known phenomenon in all such computational work.

We conclude part I here and shall give our final concluding remarks on the contents of this paper at the end of part II which follows.

PART II. — SYNOPSIS

In this part is given a quadratic potential function which, without taking anharmonicity into account, reproduces the observed frequencies fairly satisfactorily; in this problem this is regarded as a better procedure than to make the correction for anharmonicity in one or other arbitrary manner. The method used to obtain such a potential function is to observe the variation of the roots of the secular equation with a variation in the values of the potential constants and then to choose a suitable set of variations in the potential constants so as to produce the most satisfactory result. By this procedure a potential function has been obtained which gives the calculated frequencies differing from the observed values by less than 2 cm^{-1} in the great majority of the 24 frequencies.

The purpose of the calculation being to absorb the effect of the anharmonic part into the quadratic part, obviously it is not possible to produce a unique quadratic potential function; many slightly differing functions can be given producing in a qualitative way equally good results. This is further exhibited by an example where the dimensions of the molecule are in error but still we have a corresponding, fairly good, potential function. All these calculations exhibit clearly the « flexibility » inherent in the problem when the correction for anharmonicity has not been made.

The most certain utility of the Decius, Wilson sum rules lies in the possibility of checking the calculated frequencies if not always in the complete evaluation of the potential function.

10. Anharmonicity and readjustment of potential constants

If a correction for anharmonicity is possible because of extensive and accurate data being available on overtones, the difficulties we are facing now do not arise. But when this is not possible there are different ways of making the anharmonic correction in one or other *empirical* way. Without making any such correction we aim here to produce a quadratic potential function which will absorb, so to say, the effect of anharmonicity, that is, a function which will produce the observed frequencies as closely as possible. Then obviously we should not expect a unique potential function for we are aiming at a spreading out of the anharmonic part over the quadratic terms and different, slightly varied ways of doing this will produce, qualitatively speaking, a good enough potential function. Thus we should guard ourselves from concluding at the end of such a calculation that the numerical values of the potential constants we get represent something unique. This is another aspect of the fact that different empirical methods of correcting for anharmonicity lead to very widely different values of the potential constants, specially so for the non-diagnonal i.e. coupling constants. Charette and Manneback (7) have recently published a thorough calculation of the potential function for the plane vibrations of ethylene. Their main thesis is to show the important fact that even some of the diagonal constants are surprisingly sensitive to the mode of correction (always empirical) for anharmonicity while some small non-diagonal constants come out with a changed sign depending on how this correction is made. Since in our problem here we are dealing with a set of frequencies in the neighbourhood of 750 cm^{-1} we consider the following to be the best course to follow instead of introducing an uncertainty by using one or other doubtful way of correcting for anharmonicity. Thus we aim at a slight readjustment of the values of the potential constants we have, so as to produce a set of calculated frequencies as near as possible the set of observed data uncorrected for anharmonicity.

First consider the non-diagonal coefficients, f_{ij}, $i \neq j$. Of the three such coefficients, f_{12} is the most doubtful and we consider it first. We observe the effect of a stepwise variation of f_{12} on the calculated frequencies while all the other potential constants are kept unchanged. We get the following results :

with $\begin{pmatrix} 0.3293 & f_{12} & +0.160 \\ f_{12} & 0.3144 & -0.09 \\ +0.160 & -0.09 & 0.3241 \end{pmatrix}$ the frequencies for molecule 1 are

f_{12}	*Squares* of frequencies for 1 and errors with respect to observed values		
0	~0.236	~0.417	~0.526
+0.02	0.214 +7.0 %	0.443 —7.5 %	0.523 0 %
+0.03	0.204 +2 %	0.457 —4.5 %	0.520 —0.6 %
+0.04	0.195 —2.5 %	0.469 —2.0 %	0.519 —0.8 %
+0.05	~0.188 —6.0 %	~0.476 —0.6 %	~0.520 —0.6 %

This shows that in combination with the values chosen for the rest of the f_{ij}, f_{12} must be taken to be + 0.04 to achieve our present purpose which is, to repeat what has already been said, to come as near as possible all the observed values in a more or less even manner for all the frequencies.

The next step we took was a combined refinement (if at all this word is usable in the present context) of all the three non diagonal constants at the same time. We took

$$\begin{pmatrix} 0.3293 & +0.04 + x & +0.16 + y \\ +0.04 + x & 0.3144 & -0.09 + z \\ +0.16 + y & -0.09 + z & 0.3241 \end{pmatrix}$$

and constructed the following exhaustive table for molecules 1 and 8. λ_i denote the squares of the frequencies :

x, y, z	Molecule	λ_1	λ_2	λ_3	$\frac{\Delta\lambda_1}{x, y, z}$	$\frac{\Delta\lambda_2}{x, y, z}$	$\frac{\Delta\lambda_3}{x, y, z}$
$x=y=z=0$	1	0.1946	0.4675	0.5200			
	8	0.1207	0.2782	0.3037			
$x=+0.004$	1	0.1907	0.4721	0.5199	—0.97	+1.14	—0.025
$y=z=0$	8	0.1182	0.2781	0.3068	—0.615	—0.0075	+0.77
$y=+0.01$	1	0.1839	0.4595	0.5305	—1.07	—0.80	+1.05
$z=x=0$	8	0.1153	0.2821	0.2969	—0.53	+0.395	—0.68
$z=+0.01$	1	0.2050	0.4582	0.5202	+1.04	—0.94	+0.015
$x=y=0$	8	0.1266	0.2780	0.2991	+0.59	—0.012	—0.46

Assuming that the problem is at a stage (with $x = y = z = 0$) where it can be taken to be linearized we get the following set of equations from the above table :

Molecule 1
$$\Delta\lambda_1 = -0.97x - 1.07y + 1.04z$$
$$\Delta\lambda_2 = +1.14x - 0.80y - 0.94z$$
$$\Delta\lambda_3 = -0.025x + 1.05y + 0.015z$$

Molecule 8
$$\Delta\lambda_1 = -0.615x - 0.53y + 0.59z$$
$$\Delta\lambda_2 = -0.0075x + 0.395y - 0.012z$$
$$\Delta\lambda_3 = +0.77x - 0.68y - 0.46z$$

Comparing the values of λ_i obtained with $x = y = z = 0$ and the experimental values we see that the $\Delta\lambda_i$ we require are

Molecule 1 $\quad \Delta\lambda_1 = +0.0056 \quad \Delta\lambda_2 = +0.0117 \quad \Delta\lambda_3 = +0.0026$

Molecule 8 $\quad \Delta\lambda_1 = +0.0051 \quad \Delta\lambda_2 = +0.0030 \quad \Delta\lambda_3 = +0.0114$

Quite needless to say that with these values of $\Delta\lambda_i$, the two sets of linear equations for x, y, z given above are not mutually consistent. Moreover if each set is solved rigorously the values of x, y, z obtained are not acceptable because they are too large compared to the values of the coefficients themselves of which x, y, z are just the increments of first order in small quantities.

The purpose of formulating these equations was *not* to solve them rigorously but was to know how to take a suitable set of x, y, z which will bring about an all round improvement in the calculated frequencies. By careful observation of these equations it is possible to

suggest what values x, y, z should be given to produce a more or less general and even improvement in the calculated frequencies. Take for example $x = +0.005$, $y = -0.007$ and $z = +0.005$ which will make **F** as follows :

$$\begin{pmatrix} 0.3293 & 0.045 & 0.153 \\ 0.045 & 0.3144 & -0.085 \\ 0.153 & -0.085 & 3.241 \end{pmatrix}$$

From the equations given above relating the $\Delta\lambda_i$ and the x, y, z, we know that with this **F** we should get the following frequencies

Molecule 1	0.2020	0.4747	0.5126
	+0.9 %	—0.9 %	—1.9 %
Molecule 8	0.1239	0.2751	0.3105
	—1.4 %	—2.2 %	—1.5 %

To exhibit more fully the change caused by taking these x, y, z we include molecules 2 and 7 into our scheme, solve the appropriate determinantal equation and place the two results side by side as follows :

$x = y = z = 0$				$x = +0.005, y = -0.007, z = +0.005$			
$\begin{pmatrix} 0.3293 & +0.040 & +0.160 \\ +0.040 & 0.3144 & -0.090 \\ +0.160 & -0.090 & 0.3241 \end{pmatrix} \equiv \mathbf{F}_1$(say)				$\begin{pmatrix} 0.3293 & +0.045 & +0.153 \\ +0.045 & 0.3144 & -0.085 \\ +0.153 & -0.085 & 0.3241 \end{pmatrix} \equiv \mathbf{F}_2$(say)			
1	0.1946	0.4675	0.5200	1	0.2020	0.4747	0.5126
	—2.8 %	—2.5 %	—0.4 %		+0.9 %	—0.9 %	—1.9 %
2	0.1734	0.3715	0.4767	2	0.1813	0.3635	0.4838
	—3.1 %	—1.9 %	—1.4 %		+1.4 %	—4.2 %	0.0 %
7	0.1220	0.3008	0.4402	7	0.1249	0.3062	0.4391
	—4.2 %	—2.6 %	—1.5 %		—2 %	—1.0 %	—1.7 %
8	0.1207	0.2782	0.3037	8	0.1239	0.2751	0.3105
	—4.1 %	—1.1 %	—3.6 %		—1.4 %	—2.2 %	—1.5 %

Inspite of a worse value in a couple of places the general conclusion from the comparison will however be in favour of $\mathbf{F}_2$. On the whole the x, y, z chosen do improve the calculated values to a certain degree. (The middle frequency of molecule 2 becomes seriously affected going down from — 1.9 % to — 4.2 %. This is a serious thing and makes it doubtful if we can call a general improvement a situation in which this is happening in one spot !) We can say further that by anymore readjustments of x, y, z (i.e. of f_{12}, f_{23}, f_{31}) we cannot make any *real* improvement in the situation; simply we shall shift the errors in different ways from one frequency to another.

Now we consider f_{ii}. In fact a correct procedure would have been to take small increments a, b, c (say) in the f_{ii} together with x, y, z in the f_{ij}, $i \neq j$, and to tackle the problem of selecting a suitable set of a, b, c, x, y and z to bring about a general improvement. In other words we should have formulated linear equations in the six unknowns x, y, z, a, b and c. But as we have shown above we may not hope to solve the linear equations so obtained, only to use them as a guide in an empirical selection of values of x, a etc. This fact makes it easier to deal separately in a manageable number of variables (say 3 at a time) and to accomplish our purpose in more steps than one.

Working as before we get the following equations

Molecule 1
$$\Delta\lambda_1 = 0.48a + 0.49b + 0.54c$$
$$\Delta\lambda_2 = 0.40a + 0.39b + 0.17c$$
$$\Delta\lambda_3 = 0.56a + 0.22b + 0.83c$$

Molecule 8
$$\Delta\lambda_1 = 0.27a + 0.37b + 0.23c$$
$$\Delta\lambda_2 = 0.02a - 0.07b + 0.52c$$
$$\Delta\lambda_3 = 0.66a + 0.31b + 0.29c$$

(A consequence of our having assumed a linearization of the problem is that upto that approximation we need not state with what accompanying set of f_{ij}, $i \neq j$, the increments a, b, c in the diagonal terms have been taken, as long as the chosen values of f_{ij}, $i \neq j$, do not destroy the linearity of the problem).

Suppose that by means of suitable a, b, c we hope to improve upon the $\mathbf{F}_2$ already formulated. Then we require the following increments in the roots :

Molecule 1 $\quad \Delta\lambda_1 = -0.0018 \quad \Delta\lambda_2 = +0.0044 \quad \Delta\lambda_3 = +0.0100$

Molecule 8 $\quad \Delta\lambda_1 = +0.0018 \quad \Delta\lambda_2 = +0.0060 \quad \Delta\lambda_3 = +0.0046$

Since a general tendency towards these $\Delta\lambda_i$ is required by an appropriate selection of a, b, c, we say now that such a selection is not possible. It is not possible to produce a general improvement on $\mathbf{F}_2$ by a certain set of a, b, c, this result being entirely a consequence of an empirical study of the above equations.

On the other hand let us try to improve upon $\mathbf{F}_1$. Then we require the following

Molecule 1 $\quad \Delta\lambda_1 = +0.0056 \quad \Delta\lambda_2 = +0.0117 \quad \Delta\lambda_3 = +0.0026$

Molecule 8 $\quad \Delta\lambda_1 = +0.0050 \quad \Delta\lambda_2 = +0.0030 \quad \Delta\lambda_3 = +0.0115$

Let us take $a = b = c = 0.006$ then we get from the equations in a, b, c given above

Molecule 1 $\quad \Delta\lambda_1 = +0.0091 \quad \Delta\lambda_2 = +0.0058 \quad \Delta\lambda_3 = +0.0097$

Molecule 8 $\quad \Delta\lambda_1 = +0.0052 \quad \Delta\lambda_2 = +0.0029 \quad \Delta\lambda_3 = +0.0076$

i.e. on taking this a, b, c we should get for molecule 1 instead of 0.1946 (— 2.8%), 0.4675 (— 2.5 %), 0.5200 (— 0.4), the frequencies 0.2037 (+ 2 %), 0.4733 (— 1.2 %), 0.5297 (+ 1.3 %); and similarly for molecule 8 instead of 0.1207 (— 4.1 %), 0.2782 (— 1.1 %), 0.3037 (— 3.6 %) we should get 0.1259 (+ 0.1 %), 0.2811 (0 %), 0.3113 (— 1.2 %). This as a whole can be regarded as an impovement.

We have thus been led to the following $\mathbf{F}$

$$\begin{pmatrix} 0.3353 & +0.040 & +0.160 \\ +0.040 & 0.3204 & -0.090 \\ +0.160 & -0.090 & 0.3301 \end{pmatrix}$$

Rounding off the figures which hardly count in the sort of calculation we are now making, let us take

$$\mathbf{F}_3 \equiv \begin{pmatrix} 0.3350 & +0.040 & +0.160 \\ +0.040 & 0.3200 & -0.090 \\ +0.160 & -0.090 & 0.3300 \end{pmatrix}$$

For comparison we give in the following table the results before and after improvement, i.e. the frequencies calculated with $\mathbf{F}_1$ and $\mathbf{F}_3$.

$\begin{pmatrix} 0.3293 & +0.040 & +0.160 \\ +0.040 & 0.3144 & -0.090 \\ +0.160 & -0.090 & 0.3241 \end{pmatrix} \equiv \mathbf{F}_1$				$\begin{pmatrix} 0.3350 & +0.040 & +0.160 \\ +0.040 & 0.3200 & -0.090 \\ +0.160 & -0.090 & 0.3300 \end{pmatrix} \equiv \mathbf{F}_3$			
1	0.1946 —2.8 %	0.4675 —2.5 %	0.5200 —0.4 %	1	0.2033 +1.5 %	0.4758 —0.7 %	0.5264 +0.7 %
2	0.1734 —3.1 %	0.3715 —1.9 %	0.4767 —1.4 %	2	0.1812 +1.3 %	0.3764 —0.6 %	0.4844 +0.2 %
7	0.1220 —4.2 %	0.3008 —2.6 %	0.4402 —1.5 %	7	0.1269 —0.4 %	0.3063 —0.8 %	0.4478 +0.2 %
8	0.1207 —4.1 %	0.2782 —1.1 %	0.3037 —3.6 %	8	0.1256 0 %	0.2818 +0.2 %	0.3099 —1.7 %

The results of $\mathbf{F}_3$ were re-studied for a possible improvement by a slight variation of f_{ij}, $i \neq j$. From the equations formulated for x, y, z it was found that a slight improvement would result on taking $x = +0.001$ and $z = -0.001$. The results which are going to be the final after this lengthy argument based completely on an empirical manipulation of linear equations are given in the following scheme. The use of the word final is not without qualification in view of what we have said regarding potential functions obtained without correcting for anharmonicity or with a correction made not rigorously but empirically.

$$\mathbf{F} = \begin{pmatrix} 0.335 & +0.041 & +0.160 \\ +0.041 & 0.320 & -0.091 \\ +0.160 & -0.091 & 0.330 \end{pmatrix}$$

Molecule	Squares of frequencies and percentage errors		
1	0.20129 +0.5	0.47804 —0.2	0.52619 +0.7
2	0.17951 +0.4	0.37665 —0.6	0.48581 +0.5
3	0.13759 —0.4	0.38414 —0.8	0.52520 +0.9

Molecule	Squares of frequencies and percentage errors		
4	0.17116	0.37348	0.49486
	—0.7	+ 0.8	—0.2
5	0.13317	0.29945	0.45076
	—0.2	—1.6	+ 0.6
6	0.16544	0.28228	0.42823
	—0.6	+ 0.5	—0.7
7	0.12567	0.30722	0.44802
	—1.3	—0.5	+0.3
8	0.12441	0.28143	0.31152
	—1.0	0.0	—1.1

The maximum departure is —1.6 %, i.e. only 0.8 % in the frequency, the quantities given above being squares of frequencies. Out of the 24 cases only 4 are such that the error (in the square of) the frequency is $\geqslant 1$ %. In the following are given the frequencies in cm^{-1} corresponding to the above set.

Molecule	Frequencies (cm^{-1}), $\frac{obs}{cal}$, % error (if obs $\sim$ cal $> 2\ cm^{-1}$)		
1	$\frac{583}{584}$	$\frac{902}{900}$	$\frac{942}{945}$ + 0.3
2	$\frac{551}{552}$	$\frac{802}{800}$	$\frac{906}{908}$
3	$\frac{484,5}{484}$	$\frac{811}{808}$ — 0.4	$\frac{940}{944}$ + 0.4
4	$\frac{541}{539}$	$\frac{793}{796}$ + 0.4	$\frac{918}{917}$
5	$\frac{476}{475}$	$\frac{719}{713}$ — 0.8	$\frac{872}{874}$
6	$\frac{531.5}{530}$	$\frac{690.5}{692}$	$\frac{855.5}{852}$ — 0.4
7	$\frac{465}{463}$	$\frac{724}{722}$	$\frac{871}{872}$
8	$\frac{462}{460}$	$\frac{691}{691}$	$\frac{731.5}{727}$ — 0.6

10*a*. Magnitude of uncertainty after cycle of calculation is completed

This article has already been introduced in a digression made in section 9. The cycle of computation is the following :

(i) initial experimental data with dispersion δ say
(ii) S_i, P_i, Δ_i with an uncertainty depending on δ
(iii) Sum and product rules of Decius and Wilson lead to the calculation of **F** with an uncertainty
(iv) The assumed geometry of the molecule introduced through **G**
(v) The secular determinant formed out of **F** and **G**
(vi) Frequency calculated with a dispersion ϵ arising out of δ
(vii) Comparison of δ and ϵ.

From the equations in section 10 which give $\Delta\lambda_i$ for molecules 1 and 8 in terms of x, y, z and a, b, c it is found that the following is the maximum effect of the uncertainties in **F** (which is possible but improbable).

$$\left.\begin{array}{l} \pm\,\Delta\lambda_1 = 0.024 \\ \pm\,\Delta\lambda_2 = 0.025 \\ \pm\,\Delta\lambda_3 = 0.007 \end{array}\right\} \text{ for molecule 1 and } \left.\begin{array}{l} \pm\,\Delta\lambda_1 = 0.015 \\ \pm\,\Delta\lambda_2 = 0.003 \\ \pm\,\Delta\lambda_3 = 0.017 \end{array}\right\} \text{ for molecule 8}$$

But of course this is a result of a *most pessimistic* view regarding the distribution of the probable uncertainties and perhaps we are justified in reducing the above quantities by one order of magnitude. To be on the safe side we shall give here in terms of per cent the above quantities as they are together with their value reduced to 1/10.

For molecule 1 :

$(\Delta\lambda_1)^{1/2} \sim \pm$ (0.6 to 6) %, $(\Delta\lambda_2)^{1/2} \sim \pm$ (0.3 to 2.6) %, $(\Delta\lambda_3)^{1/2} \sim \pm$ (0.07 to 7) % while the experimental uncertainty is $\sim \pm$ 0.16 % $\sim \pm$ 0.11 % and $\sim \pm$ 0.09 % respectively.

For molecule 8 :

$(\Delta\lambda_1)^{1/2} \sim \pm$ (0.6 to 6) %, $(\Delta\lambda_2)^{1/2} \sim \pm$ (0.05 to 0.5) %, $(\Delta\lambda_3)^{1/2} \sim$ (0.3 to 2.7) % while experimentally they are $\sim \pm$ 0.22 %, $\sim \pm$ 0.14 % and $\sim \pm$ 0.13 % respectively.

11. Possibility of giving more than one potential function

It is needless to say that the method of calculation followed upto now cannot possibly lead us to a unique potential function. The

slightly different potential functions that one can arrive at are nothing but a reflection of the fact that the spreading of the anharmonic correction over the quadratic terms can be accomplished in many different ways differing slightly from one another.

The results given and the technique shown in section 10 in such detail were of course not spontaneous but a result of much trial and error. In the course of the work many possibilities for the components of **F** were tried. Glossing over the details as to how exactly the f_{ij} were obtained we only give the result for molecules 1, 2, 7, 8.

With $\begin{pmatrix} 0.3377 & 0.0366 & 0.1659 \\ 0.0366 & 0.3224 & -0.0943 \\ 0.1659 & -0.0943 & 0.3329 \end{pmatrix}$ we get

1	0.2001	0.4744	0.5361
	0 %	—0.8 %	+2.6 %
2	0.1775	0.3853	0.4830
	—0.8 %	+ 1.8 %	0 %
7	0.1260	0.3049	0.4527
	—0.8 %	—1.6 %	+ 1.4 %
8	0.1244	0.2862	0.3079
	—0.8 %	+2 %	—2.4 %

Qualitatively speaking this result is certainly not so good as that given by the « final » **F** but compared with the result from $\mathbf{F}_1$ or $\mathbf{F}_2$ it is as good if not better. As can be seen the potential coefficients are considerably different.

12. Effect of changed dimensions

The nine dimensional parameters which determine the six elements of the **G** matrix can be made to play the same role as the elements of **F** in the above treatment; in other words, for a slightly changed geometry of the molecule we can produce an **F** again giving qualitatively the same results as the final **F** given in section 10.

During the course of the work, an accidental error was introduced which in effect amounted to an assumed geometry which gave the moments of inertia different from the values of Cornwell for C_2H_3Br. This geometry was as follows :

C—H distances = 1.07 Å

$\widehat{CCH}$ angles = 120°

C—Br distance = 1.868 Å

CCBr angle = 124°30′

giving $I_C = 131.2209$ and $I_A \times I_B = 1088.282$ instead of Cornwell's $I_C = 131.19$ and $I_A \times I_B = 1145.39$

We shall state the results of our calculations with these dimensions; the **F** taken was

$$\begin{pmatrix} 0.3282 & +0.04055 & +0.1611 \\ +0.04055 & 0.3136 & -0.08766 \\ +0.1611 & -0.08766 & 0.32245 \end{pmatrix}$$

giving the following for squares of frequencies and the percentage errors in the squares as compared with experiment

1	0.2009	0.4633	0.5194
	+ 3.5	— 3.5	— 0.6
2	0.1804	0.3679	0.4754
	+ 0.9	— 2.9	— 1.7
3	0.1374	0.3719	0.5189
	— 0.6	— 4.1	— 0.2
4	0.1720	0.3685	0.4804
	— 0.2	— 0.3	— 3.2
5	0.1338	0.2910	0.4436
	+ 0.3	— 4.3	— 0.9
6	0.1669	0.2790	0.4153
	+ 0.3	— 0.7	— 3.7
7	0.1265	0.3002	0.4388
	— 0.6	— 3.0	— 1.8
8	0.1256	0.2779	0.3022
	— 0.1	— 1.1	— 4.3

This result is, qualitatively speaking, the same as that given by $\mathbf{F}_1$ of section 10 for example, though not so good as the one called the « final » **F**. This is additional material for the « fluidity » of the problem dealt with in the following section 13.

13. The flexibility of the problem

The peculiar difficulties which we have come accross in the above calculation are a consequence of the fact that mathematically the

problem is not quite determinate. The considerable amount of « play » that can be allowed to the potential constants, specially the non-diagonal ones, and also to the dimensions of the molecule is a consequence of the fact that our purpose has been to reproduce, by calculation, the observed frequencies uncorrected for anharmonicity; counting the parameters in the problem, there are 9 dimensional parameters, 6 quadratic potential coefficients and 15 quartic potential constants (if coupling with the planar motion is neglected). Hence what we have tried to do is to absorb the effect of the 15 parameters of anharmonicity (in fact more) into the 9 dimensional and 6 quadratic constants, mainly into the latter. [Perhaps 15 is rather too strenuous a condition, one might say instead, the six parameters appearing in the energy of vibration when the motion is regarded as anharmonic].

The best hope for the future is the procurement of extensive and accurate data on the overtones from a spectrum dispersed by a grating enabling us to make a reasonable correction for anharmonicity. Once that is correctly done of course there remains no room for the discussion given in this paper.

The initial attempt at the correction due to anharmonicity will obviously be not in the direction of a complete theoretical evaluation of each anharmonic coefficient in the energy in terms of those in the potential but rather to evaluate them from the data on overtones and to correct the observed fundamentals for anharmonicity. It is improbable that the former effort is really worth the complicated integrations and will ever be made but as to the latter all that we need is a more exact evaluation of the band centres of the fundamentals and of the second harmonics by a detailed analysis of the vibration-rotation spectrum dispersed by a grating spectrograph. This should be done in the region, apart from that of the fundamentals, of 1000-2000 cm^{-1} for C_2H_3Br and of 900-1500 cm^{-1} for C_2D_3Br. It is not necessary that every molecule of the set be so treated, for the anharmonic coefficients of isotopic molecules, upto a certain approximation, are interrelated, information on molecules 1 and 8 should suffice for a fairly satisfactory correction throughout the set.

Perhaps we can make certain plausible guesses as to the direction in which the rigorous quadratic potential constants will differ from the ones called the « final » values in section 10. The *differential* anharmonicity between adjacent molecules can hardly be more than about one or two per cent and since the f_{ii} obtained from the sum rules have already been stepped up by about that amount it looks

fairly certain that the values of the f_{ii} occurring in the rigorous quadratic potential could not be different from the « final » f_{ii} of section 10 by more than about 1 or say 2 %. But regarding f_{ij}^2, $i \neq j$, we can hardly say the same. A glance at the equation in section 7 giving f_{ij}^2 shows that corresponding to a change of a couple per cent in the other quantities occurring in these equations, f_{ij}^2 will be violently affected, even to the extent of 50 to 100 %. Taking of the square root will change matters but little.

These results show that the burden of the uncorrected anharmonicity is carried more or less completely by the non-diagonal constants; this agrees with recent work on C_2H_4(7). The most pessimistic point of view would be to say that even the signs of the f_{ij} (at least of some of them) remain doubtful; as a proof one might point out that the equations determining the signs of some of the f_{ij} are extremely sensitive to small variations in the data supplied and hence the behaviour of these equations after the (rather drastic) anharmonic correction has been made becomes unpredictable. On the other hand a less pessimistic point of view would be to say that for a satisfactory averaging out of the anharmonic effect it is necessary to take the signs as they have been taken in the « final » **F** of section 10 and this averaging could not be of an amount more than a few percent; hence the sign of quantities whose numerical value is not small at all may be expected to be conserved when this averaging has been taken account of by applying the anharmonic correction.

14. Checking the calculated frequencies :

After having chosen a particular ' **G** ' and ' **F** ' one has to set up the secular equation, then expand it as a polynomial and then determine the roots which give the squares of the frequencies. One would like to have a simple check for this considerable numerical work, a check which is not simply a repetition of every calculation twice over. For this purpose the identities we formulated in section 5 are most useful. *One can even say in a very general way that these identities will always have a guaranteed usefulness even though due to one reason or another they may not be found very useful in calculating the potential constants; this use of the identities is their ability to form a numerical check on the calculated frequencies.*

Consider the calculated frequencies using the final **F** of section 10.

From these we get the following S, P, Δ on which the identities can be applied. We have

	S	P	Δ
1	1.20552	0.45368	0.050632
2	1.04197	0.33780	0.0328465
3	1.04693	0.32687	0.027759
4	1.03950	0.333445	0.031633
5	0.88338	0.23489	0.017976
6	0.87595	0.23843	0.019999
7	0.88091	0.23255	0.017297
8	0.71736	0.16144	0.010907

From the above figures :

$$S_1 - S_4 = 0.16602; \quad S_1 - S_3 = 0.15859; \quad S_1 - S_2 = 0.16355$$
$$S_2 - S_6 = 0.16602; \quad S_2 - S_5 = 0.15859; \quad S_3 - S_5 = 0.16355$$
$$S_3 - S_7 = 0.16602; \quad S_4 - S_7 = 0.15859; \quad S_4 - S_6 = 0.16355$$
$$S_5 - S_8 = 0.16602; \quad S_6 - S_8 = 0.15859; \quad S_7 - S_8 = 0.16355$$

$$P_1 - P_3 - P_4 + P_7 = 0.02592; \qquad P_2 - P_5 - P_6 + P_8 = 0.02592$$
$$P_1 - P_4 - P_2 + P_6 = 0.02087; \qquad P_3 - P_7 - P_5 + P_8 = 0.02087$$
$$P_1 - P_2 - P_3 + P_5 = 0.02390; \qquad P_4 - P_6 - P_7 + P_8 = 0.02391$$

This checks the calculated frequencies, the numerical part of the calculation (with « final » **F**) is thus without error. This exhibits the usefulness of the identities formulated in section 5, the sum rules of Decius and Wilson.

15. Physical meaning of potential constants from two points of view

The internal coordinates we have been using are simply the distances of the H, D nuclei from the skeleton plane. The potential we have arrived at is

$$2V = (Q_\alpha\ Q_\beta\ Q_\gamma) \begin{pmatrix} 0.335 & +0.041 & +0.160 \\ +0.041 & 0.320 & -0.091 \\ +0.160 & -0.091 & 0.330 \end{pmatrix} \begin{pmatrix} Q_\alpha \\ Q_\beta \\ Q_\gamma \end{pmatrix}$$

where α, β, γ are as in the diagram of section 3.

The potential constants give the following information; (1) the force required to pull out either of α, β, γ out of the plane while

the rest of the five are strained to remain in the plane is very nearly the same. (II) When α is pulled out upwards from the plane of the paper, β and γ both tend to get pushed downwards below the plane, the latter with a force about 4 times larger than the former. (III) when β is pulled out of the plane, α of course is pushed downwards while γ gets pulled out by a force more than twice as big.

The result that α and γ are more intensely coupled seems peculiar since in the molecule their distance is larger than that between either of the pairs α, β or β, γ. In fact the numerical value of the coupling constant varies contrary to the variation of the distance; the nearest α, β have the smallest coupling constant while the farthest α, γ have the largest of the three.

These facts as they stand seem to give no really useful information regarding the structural characteristics of the molecule in question. But when we apply the following transformation of internal coordinates we find the position much changed.

Let us write 2 V in terms of (I) the elevation of the mid point of line α β out of the skeleton plane, (II) the twist of the CH_2 radical round the C — C axis, and (III) as before the distance of γ from the skeleton plane. If we call these respectively Q_1, Q_2 and Q_3 we can write

$$Q_1 = (Q_\alpha + Q_\beta)/2 \quad , \quad Q_2 = (Q_\alpha - Q_\beta)/2 \quad , \quad Q_3 = Q_\gamma \qquad \text{or}$$

$$Q_\alpha = Q_1 + Q_2 \quad , \quad Q_\beta = Q_1 - Q_2 \quad , \quad Q_\gamma = Q_3$$

This transformation of coordinates gives instead of **F** the following :

$$2V = (Q_1 Q_2 Q_3) \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0.335 & +0.041 & +0.160 \\ +0.041 & 0.320 & -0.091 \\ +0.160 & -0.091 & 0.330 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}$$

$$= (Q_1 Q_2 Q_3) \begin{bmatrix} 0.335 + 0.320 & 0.335 & 0.160 \\ +0.041 + 0.041 & -0.320 & -0.091 \\ 0.335 & 0.335 + 0.320 & 0.160 \\ -0.320 & -0.041 - 0.041 & +0.091 \\ 0.160 & 0.160 & 0.330 \\ -0.091 & +0.091 & \end{bmatrix} \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix}$$

$$= (Q_1 Q_2 Q_3) \begin{pmatrix} 0.737 & +0.015 & +0.069 \\ +0.015 & 0.573 & +0.251 \\ +0.069 & +0.251 & 0.330 \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}$$

The reason for writing the transformed matrix first in an analytical form is to see how the various quantities in the transformed matrix arise out of the initial f_{ij}.

We note for example that the coupling constant + 0.015 arises out of the difference $f_{11} - f_{22}$ which from the sum rules is found to be $k\ (S_3 - S_4)$ or $k\ (S_5 - S_6)$. The requirement $S_3 - S_4 = S_5 - S_6$ is excellently obeyed as seen from the following.

$$S_3 - S_4 = 0.0073, \qquad S_5 - S_6 = 0.0075$$

It seems safe to say that these differences will retain their sign when the correction for anharmonicity is made i.e. + 0.015 will retain its sign though certainly not the last significant figure.

It can similarly be observed how the signs and magnitudes of the various f_{ij} affect the values of the constants in the transformed matrix.

Conclusion

There are two aspects of the long calculation we have made above. Firstly the fact of having obtained a potential function which, together with the geometry assumed, (partly on the basis of experimental data), gives the 24 observed gauche frequencies of the 8 molecules of the isotopic set $C_2H_3Br - C_2D_3Br$, to a satisfactory degree of accuracy; and secondly the difficulties encountered in this calculation mainly due to our ignorance of the anharmonic correction for each of the frequencies.

It has been the usual argument in such calculations made by previous authors that, in view of the large number of frequencies accounted for by means of a comparatively small number of parameters, the actual numerical values of these parameters (i.e. the potential constants) have a degree of reliability. We wish to emphasise in this context our observations made in the above paper regarding the possibility of giving a number of potential functions with considerably different values of the constants (specially the coupling coefficients) which give a calculated set of frequencies qualitatively very similar to one another. Specially so will be the case where due to reasons of complexity or otherwise a particular « physically constructed » potential function, instead of the general one is used, e.g. with the supposition of valence or central forces. When such a potential

function has been obtained we should be specially careful not to put undue emphasis on the numerical values of the constants.

Regarding the sum and product rules of Decius and Wilson, we can say that even though very well obeyed throughout the data provided experimentally they fail to give us the potential constants with a finality which appears at first sight. They certainly are an excellent test for the quality of the data provided and for the identification of frequencies where this is doubtful. As shown in section 14 *a* of our paper, these rules will always find excellent use in the checking of extensive computational work.

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